Catalytic Pathways and Periodic Reactivity Trends for the Hydrogenation of Acetic Acid in Condensed Phase on Transition Metal Clusters

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Introduction

Catalytic hydrogenation of light carboxylic acids and aldehydes forms alcohols, which act as alkylating agents in reactions with phenolic compounds (phenol, catechol) to produce aromatic fractions with higher heating values. Hydrogenation of carboxylic acids requires successive H addition into the C=O while leaving the C-C intact, thus preventing carbon losses from the liquid products. The catalytic pathways and periodic reactivity trends for these reactions, which occur in parallel, in the aqueous phase have not been rigorously established and confirmed by experiments. Herein, we interrogate the sequential and concomitant C-H insertion, C-C dissociation, and C-O cleavage during the reactions of acetic acid, the simplest and most abundant light organic acid contained in bio-oil, with hydrogen on nanometer-sized transition metal clusters (Fe, Ni, Ru, Pd, Pt) based on rate measurements, kinetic modeling, and isotopic studies. We describe the catalytic pathway, propose a sequence of elementary steps and their kinetic relevance, and then establish the relation of rate constant values and the thermodynamic quantities of transition metal clusters. We derive from these data the periodic reactivity and selectivity trends for H insertion into the C=O and for the competing C-C cleavage steps. The knowledge of catalytic properties and their function is used to guide the design of stable and selective catalysts used for catalytic tuning to realize the one-pot hydrogenation-alkylation synthesis of aromatics while preventing carbon losses from the liquid into the gas phase.

Materials and Methods

Incipient wetness impregnation was used to prepare transition metal (5 wt.% Fe, 5 wt.% Ru, 10 wt.% Ni, 5 wt.% Pd, 5 wt.% Pt; 7-35 % dispersion) catalysts supported on activated carbon. Catalytic rates and selectivities for aqueous phase hydrogenation of acetic acid were obtained with 50-200 mg of catalyst in a batch reactor (300 cm³, Parr Instrument 4560) at 30-50 bar H₂ pressures and 433–543 K for a duration of 60–6000 min. Chemical compositions in the liquid and gas phases were quantified by gas chromatograph.

Results and Discussion

Aqueous phase hydrogenation of acetic acid on transition metal clusters at 50 bar H₂ (0.81 H₂O/H₂) and 413-543 K shows five orders of magnitude difference in turnover rates (normalized by exposed metal sites, 0.02-4500 h⁻¹) and forms ethanol, ethyl acetate, methane, and ethane (carbon selectivities 20-90 %, 3-17 %, 4-67 %, and 2-11 %, respectively). Ethanol, the desired product, may undergo decomposition and lead to the formation of methane and ethane. It may also undergo Fischer esterification reactions with acetic acid to form ethyl acetate. The time-dependent evolution of the chemical species in both liquid and gas phases for reactions with acetic acid-H₂, ethyl acetate-H₂, ethanolic-H₂ together with reactions in D₂O mixtures, led us to propose a series of the reaction pathways in Figure 1a. Acetic acid is activated via an initial C-O scission step (Figure 1a, Step 1) that resulted in an adsorbed acetyl and hydroxyl species, also reported in density functional theory calculations [1-3]. Sequential insertion of H atoms derived from H₂ dissociation into the acetyl species via surface acetaldehyde and leads to ethanol (Step 2). The acetyl species may also undergo competitive C-C bond cleavage and hydrogen insertion to form methane (Step 3). The temperature effects on site time yield of ethanol are shown in Figure 1b. Over the series of catalysts, effective barriers for C-C bond cleavage leading to methane formation are larger than for H addition steps (e.g. 84 kJ mol⁻¹ vs. 59 kJ mol⁻¹ for 413-483 K on Ru). Thus, the undesired C-C bond cleavage step depends more sensitively on temperature than the initial H addition step. As temperature increases to above 483 K, turnover rates for both reactions depend less on temperature (Figure 1b). This transition in the effective activation barrier appears to be general for the series of catalysts and may reflect the destruction of catalytic sites, possibly through leaching of the metal from carbon supports in the high temperature acidic medium.

Product composition and selectivity (Table 1) reveals that within the same group of the periodic table, acetic acid conversion rates increase with increasing atomic number (Fe < Ru; Ni < Pd < Pt). Within the first row, Fe and Ni exhibit similar rates and selectivities. Elements in the second row, however, show different catalytic rates: Ru promotes acetic acid conversion and methane formation more effectively than Pd. The periodic reactivity trends and the kinetically relevant steps are directly related to the carbon binding strengths. For Ru, Ni, Pd, and Pt, the dissociative adsorption of acetic acid to surface acetyl species is the kinetically relevant step. Rates increase with increasing metal-carbon binding strength (Ru>Pt>Pd>Ni) [4]. For Fe, further increase in the carbon binding strength leads to decreased rates, suggesting strong binding of acetyl species on Fe inhibits the acetic acid turnovers. The ethanol selectivity is controlled by the reversible acetyl hydrogenation step and acetyl dissociating further to surface methyl. For Ru, Pt and Pd, the reversed ethanol decomposition (Figure 1a, Step 4) is also favored [5], which led to a lower selectivity to ethanol compared to Fe and Ni.

Significance

Catalytic hydrogenation of acetic acid on dispersed transition metal clusters in aqueous phase forms ethanol and light alkanes via competitive H addition and the C-C bond cleavage routes at rates and selectivities that are mediated by the binding strengths of carbon to transition metal surface.

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References