Acetic Acid Adsorption and Reactions on Pt and Ni

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Introduction

Pt and Ni-based catalysts are actively studied in the development of improved technologies for the conversion of biomass-derived feedstocks into fuels and chemical intermediates, specifically for hydrodeoxygenation and steam reforming of bio-oils. Since acetic acid is a component of bio-oils as well as a widely used model compound, it is important to better understand its reactivity on Pt and Ni catalytic surfaces at the molecular level. Our previous study determined surface species and reactions for acetic acid on Ni(110). [1] In this work, catalytic performance of silica-supported Ni and Pt catalysts was compared in acetic acid hydrodeoxygenation in a fixed-bed flow reactor. Reasons for the observed catalytic differences at the molecular level were studied by comparing acetic acid adsorption and reactions on well-defined single-crystal surfaces of Ni(111) and Pt(111) with infrared reflection absorption spectroscopy (IRAS), temperature-programmed desorption (TPD) and density functional theory (DFT) calculations.

Materials and Methods

5 wt % Pt/SiO_2 and 1.5 wt % Ni/SiO_2 catalysts (equivalent molar metal loadings) were prepared using an incipient wetness impregnation method. The catalysts were dried at 393 K and then calcined at 723 K. Prior to testing, the catalysts were reduced at 523 K in situ. Acetic acid hydrodeoxygenation was performed in a gas-phase flow reactor at 473-573 K with online sampling using a gas chromatograph, similarly to our previous study of Pt-Mo catalysts [2]. TPD experiments for acetic acid adsorption on Pt(111) were performed in a three-level, stainless-steel ultrahigh vacuum (UHV) chamber, with the sample in the line of sight of the ionizer of a shielded UTI 100C quadrupole mass spectrometer. IRAS spectra were collected in a separate UHV chamber using a Bruker Vertex 70 instrument with a grazing incidence of 75° from the surface normal and a liquid nitrogen cooled mercury-cadmium-telluride detector. Gradient-corrected periodic DFT calculations with the DMol^3 code using the GGA-PW-91 functional and the DNP basis set were performed for determining geometries, adsorption energies and vibrational frequencies for acetic acid and its reaction products on Ni(111) as well as on Pt(111), the same single-crystal surface that was used in the experimental TPD and IRAS measurements.

Results and Discussion

Experimental IRAS spectra and TPD results as well as DFT computational results show that acetic acid adsorption and reactions on Pt and Ni surfaces are similar. The O-H bond in molecularly adsorbed acetic acid breaks to form bridge-bonded bidentate acetate that becomes the dominant surface species at low temperatures (Figure 1). At higher temperatures, the surface acetate and other hydrocarbon surface species decompose on both Pt and Ni (Figure 2). Despite the similarities in acetic acid adsorption and reactivity in surface science experiments, the catalytic reactor performance of Pt and Ni in acetic acid hydrodeoxygenation is significantly different. The activity of Ni is lower than that of Pt. The lower catalytic activity of Ni is attributed to its lower reducibility. Although Pt and Ni surfaces can both efficiently adsorb acetic acid and split its C-O bonds once, Ni, in contrast with Pt, cannot be easily reduced to remove the generated surface oxygen. It is, thus, not the surface reactivity of acetic acid, but the lower reducibility of Ni that limits the catalytic cycle.

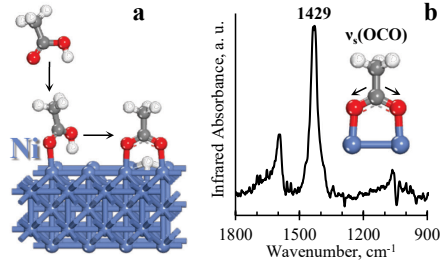

Figure 1. (**a**) Structures for molecularly adsorbed acetic acid and bidentate acetate surface species on Ni obtained with DFT calculations, (**b**) IRAS spectrum with a characteristic vibration for bidentate acetate surface species on Ni.

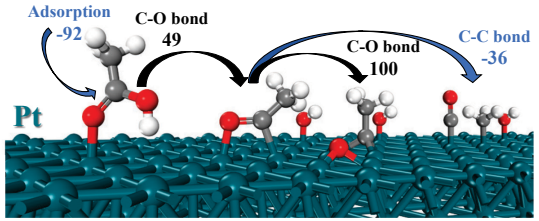

Figure 2. Surface species and reaction energies for C-O and C-C bond splitting reactions for acetic acid on Pt obtained with DFT calculations.

Significance

Acetic acid adsorption and reactivity on Pt and Ni were compared at the molecular level. Although acetic acid adsorption and surface reactions on both metals are similar, the catalytic activity of Ni is lower due to its lower reducibility. These findings will be useful in the development of more efficient catalysts for upgrading of bio-mass derived feedstocks.

References

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2. Zheng, Y., Tang, Z., Podkolzin, S. G. *Chem. - Eur. J.* 26, 5174-5179 (2020).