Communication

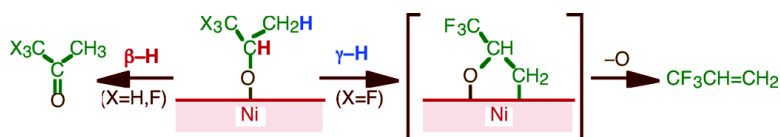# Switching of Alcohol Oxidation Mechanism on Nickel Surfaces by Fluorine Substitution

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Switching of Alcohol Oxidation Mechanism on Nickel Surfaces by Fluorine Substitution

Qing Zhao and Francisco Zaera*

Department of Chemistry, University of California−Riverside, Riverside, California 92521

Received May 22, 2003; E-mail: francisco.zaera@ucr.edu

It can be safely said that one of the most important issues in heterogeneous catalysis today is selectivity.[1] This is particularly critical in hydrocarbon oxidations, where thermodynamics predicts the production of carbon dioxide and water;[2] useful partial oxidation compounds can only be made via kinetic control.[1,3] With organic alcohols, competition is often seen among dehydrogenation, decarbonylation, and dehydration reactions.[4−6] We have previously shown that alcohols can be selectively dehydrogenated to aldehydes or ketones on nickel catalysts.[7−9] Here we report results from experiments using model nickel surfaces that indicate a partial switch from alcohol dehydrogenation to alcohol dehydration driven by substitution of γ-hydrogens with more electronegative fluorine atoms.

Temperature-programmed desorption (TPD) experiments were carried out on a Ni(100) single crystal by using a stainless steel ultrahigh vacuum (UHV) chamber evacuated with a turbomolecular pump to a base pressure of less than 1×10^{-10} Torr and equipped with instrumentation for TPD and other surface-sensitive spectroscopies.[10,11] The nickel crystal was spot-welded to an x−y−z manipulator via tantalum support wires in contact with a liquid nitrogen reservoir for cooling and/or resistively heating to any temperature between 90 and 1200 K, as monitored with a chromel−alumel thermocouple spot-welded to the edge of the crystal. The surface was cleaned periodically by cycles of oxygen treatment, Ar$^+$ ion bombardment, and annealing to 1200 K until no impurities were detected by TPD or XPS. TPD data were obtained by heating the crystal at a linear heating rate of 10 K/s, set by a homemade temperature controller, while sequentially recording partial pressures for up to 15 masses at a time using a computer-interfaced mass spectrometer. The 2-propanol (99.9% purity), 1,1,1-trifluoro-2-propanol (97% purity), and all other chemicals listed in Table 1 were purchased from Aldrich, subjected to several freeze−pump−thaw cycles before use, and routinely checked by mass spectrometry. Saturated monolayers were assured by dosing the clean nickel surface with 5.0 Langmuirs (1 L = 1×10^{-6} Torr s) of the appropriate compound at 100 K.

The key results from these studies are summarized in Figure 1. It has been well established that alcohols, either coordinated to metal centers[12] or adsorbed on metal surfaces,[6] usually undergo an initial and early dehydrogenation step at the hydroxyl position to form an alkoxide intermediate. It has also been determined that on late transition metals those alkoxides later follow a β-hydride elimination to the corresponding aldehyde or ketone.[5,13] The left panel of Figure 1 indicates that this mechanism holds true for the case of 2-propanol on Ni(100) and that a substantial fraction of that adsorbate desorbs as acetone around 325 K.[7,9] Although a small amount of propene is also seen about 220 K, this is the result of a complex bimolecular reaction involving hydrogen-bonded adsorbed species[14,15] and is not relevant to this discussion. Monolayer molecular desorption takes place at 212 K.

The right panel of Figure 1 displays the corresponding TPD results for 1,1,1-trifuoro-2-propanol on Ni(100). Here, the replace-
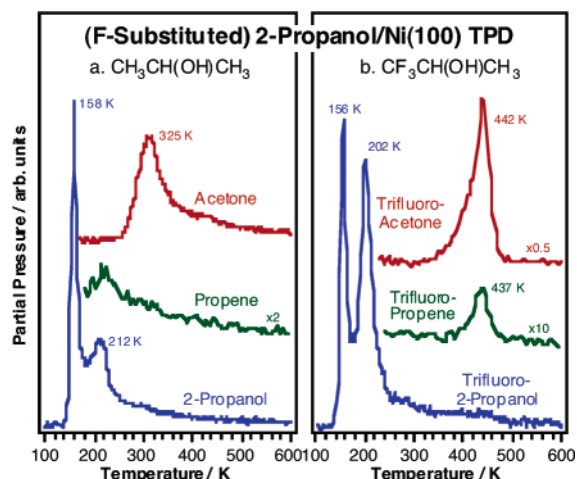

Figure 1. Temperature-programmed desorption (TPD) data for saturation coverages of 2-propanol (left) and 1,1,1-trifluoro-2-propanol (right) on Ni(100) single-crystal surfaces. Shown in both cases are traces for molecular desorption and for the products of dehydration (alkene) and dehydrogenation (ketone) reactions. The inductive effect exerted by fluorine atoms substituted at the γ-position leads to a significant inhibition of β-hydride elimination from the alkoxide intermediates and to the opening of a new γ-hydride elimination channel that eventually ends in alkene formation.

ment of hydrogens by more electronegative fluorine atoms in one of the γ-carbons of the alcohol was used to slow the β-hydride elimination step reported above. Fluorine substitution has already been used successfully to stabilize alkoxide ligands both in organometallic complexes[16] and on metal surfaces.[17] The data in Figure 1 show that this approach also works for the system studied here: 1,1,1-trifluoroacetone desorption from 1,1,1-trifluoro-2-propanol peaks at 442 K, a temperature more than 100 K higher than that seen for acetone production from 2-propanol. Moreover, the shape of the 1,1,1-trifluoroacetone peak corresponds to zero-order kinetics, suggesting that the reaction takes place at surface defects and is limited by surface diffusion of the reactants to those sites. This means that fluorine substitution at the γ-position of the alcohol leads to an increase in activation energy for β-hydride elimination of approximately 10 kcal/mol. It should be pointed out that this difference is not due to changes in the adsorption energy of the reactant, estimated from the 212 and 202 K TPD peaks in Figure 1 to be 11.4 and 10.8 kcal/mol for regular and 1,1,1-trifluoro-2-propanol, respectively.[18] Inhibition of the β-hydride elimination step upon fluorine substitution allows for the opening up of a second pathway for the adsorbed alcohol, a dehydration reaction. This is seen in the TPD data in Figure 1 as a 3,3,3-trifluoropropene desorption peak at 437 K. Previous reports have shown that selectivity in alcohol conversion on metals can be modified by coadsorption of electronegative atoms such as oxygen and sulfur on the surface.[19] However, this is, to the best of our knowledge, the first report of such a switch in selectivity due to inductive effects within the reacting molecule.

Table 1. TPD Temperature Maxima for Selected Dehydrogenation Steps on Ni(100) Surfaces[a]

reactant	product	TPD T_{max} (K)	E_a (kcal/mol)	reaction
ethanol	acetaldehyde	302 ± 3	16.4	β-H elimination
1-propanol	propanal	290 ± 3	15.8	β-H elimination
2-propanol	acetone	325 ± 3	17.7	β-H elimination
1,1,1-F$_3$-2-propanol	1,1,1-F$_3$-acetone	442 ± 2	24.4	β-H elimination
tert-butyl bromide	isobutene	242 ± 2	13.1	β-H elimination
tert-butyl chloride	isobutene	240 ± 2	13.0	β-H elimination
tert-butyl chloride-d_9	isobutene-d_9	241 ± 3	13.0	β-H elimination
tert-butyl thiol	isobutene	375 ± 3	20.6	γ-H elimination
neo-pentylidene	isobutene	387 ± 2	21.3	γ-H elimination
neo-pentylidene-γ-d_9	isobutene-d_9	406 ± 2	22.3	γ-H elimination
tert-butyl bromide[b]	isobutene	420 ± 10	23.1	γ-H elimination
tert-butyl chloride-d_9[b]	isobutene-d_9	430 ± 10	23.7	γ-H elimination
tert-butyl amine[b]	isobutene	430 ± 10	23.7	γ-H elimination
tert-butyl alcohol	isobutene	430 ± 2	23.7	γ-H elimination
tert-butyl alcohol-d_{10}	isobutene-d_9	445 ± 3	24.6	γ-H elimination
1,1,1-F$_3$-2-propanol	3,3,3-F$_3$-propene	437 ± 5	24.1	γ-H elimination

[a] Activation energies were estimated from these by using Redhead's Equation[18] and assuming first-order kinetics and a preexponential factor of 1×10^{12} s^{-1}. [b] Minor reaction channel.

The question remains as to the mechanism for the alcohol dehydration reported here. It has already been demonstrated that 2-propanol chemisorbed on Ni(100) dehydrogenates at low temperatures to produce 2-propoxide surface species.[9] We contend that the rate-limiting step in the dehydration process is a subsequent dehydrogenation from the γ-position of the propoxide to yield a surface oxamatallacycle; fast oxygen elimination from that intermediate then produces the final olefin. Evidence for this assertion is provided in Table 1, which provides a summary of results from TPD experiments with a family of related compounds on Ni(100) surfaces. The first three entries show the small effect that methyl substitutions at either the β- or γ-positions have on the activation barrier of β-hydride elimination from adsorbed alcohols, negligible compared to the differences between alcohol dehydrogenation and dehydration reactions. Next, data are provided for the production of isobutene from a number of *tert*-butyl compounds. Halohydrocarbons have been shown to undergo a facile carbon–halogen scission step on metal surfaces and to produce the corresponding surface alkyl group below 200 K;[10,20] the resulting isobutyl surface intermediate in those cases loses a β-hydrogen around 240 K to yield isobutene.[21] On the other hand, *tert*-butyl thiol, *tert*-butyl amine, and *tert*-butyl alcohol all produce isobutene at much higher temperatures, above 375 K. This is also true for neopentylidene[22] and for minor fractions of *tert*-butyl bromide and *tert*-butyl chloride-d_9. The high temperature of this process, the lack of a strong correlation between the nature of the heteroatom in the reactant and the isobutene desorption temperature, and the kinetic isotope effect seen between *tert*-butyl alcohol and *tert*-butyl-alcohol-d_{10} all point to γ-dehydrogenation preceding the C–X bond-breaking step.

Surface oxametallacycles have been prepared previously by decomposition of β-halo alcohols[14,23] and proven to decompose on Ni(100) to the corresponding olefin.[15] On the other hand, alkene formation via dehydration of adsorbed alcohols is more typical with reactive early transition metals.[5] In catalysis, alcohol dehydration is usually carried out using acidic oxides.[4] Here we have shown that a different mechanism can opened up for that process on late transition metals because of inductive effects. This pathway relies on a competition between β- and γ-hydride elimination steps. The definition of catalytic selectivity by the regioselectivity of a dehydrogenation step has already been documented for alkyl groups[1,24] and may very well be quite general for many catalytic processes involving hydrocarbons.

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JA0362858