Hydrocarbon Oxidation, Dehydrogenation and Coupling over Model Metal Oxide Surfaces

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Objectives

The overall goal of the project is to develop an understanding of structure/function relationships in small alkane oxidation and dehydrogenation over transition metal oxide surfaces.

Technical Barriers

Selective heterogeneous catalysts for the dehydrogenation of ethane are limited by the equivalent C–H bonds which show no selectivity in ethane activation. A clear understanding of the elementary chemical steps in the reaction of the different possible intermediates may help us overcome these difficulties.

Abstract

The reaction of C_1 hydrocarbon fragments has been examined on α-$Cr_2O_3(10\bar{1}\bar{1}2)$, α-$Cr_2O_3(0001)$, α-$Fe_2O_3(10\bar{1}\bar{1}2)$ and manganese oxides. The material choices allow some separation of structural and electronic effects, and an examination of the surface chemistry of oxides with $3d^3$, $3d^4$ and $3d^5$ transition metal 3+ cations.

Progress Report

Work in past project periods has focused on understanding the reactivity of different C_1 and C_2 hydrocarbon surface intermediates that may play an important role in ethane dehydrogenation over transition metal oxide surfaces. Most recently we have focused on the C_1 species, methyl and methylene, because they show an important range of reactivity related to dehydrogenation, surface diffusion, and coupling reactions (carbon-carbon bond making). Our goal has been to understand both structural and electronic effects in the reactions of these species

Chromia Surfaces

Chromia was chosen as a target material because it exhibits an ability to selectively dehydrogenate butanes to butylenes, although the selectivity for ethane dehydrogenation or oxidative dehydrogenation is limited. For butane dehydrogenation, coordinately unsaturated Cr^{3+} centers are thought to be the primary reaction sites for the dehydrogenation chemistry.

Reactions were studied on the α-$Cr_2O_3(10\bar{1}\bar{1}2)$ and α-$Cr_2O_3(0001)$ surfaces to examine the structure sensitivity of the methyl, CH_3, dehydrogenation reaction and the diffusion and coupling of methylene, :CH_2, to ethylene, CH_2=CH_2. These chromia surfaces, because of the $3d^3$ electronic configuration of the Cr^{3+} cations, are highly nonreducible in UHV, even when exposed to hydrogen atoms. As a result, no oxygen-containing products are observed in TPD from these surfaces.

The $(10\bar{1}\bar{1}2)$ and (0001) surfaces expose Cr^{3+} cations with coordination numbers of five (one coordination vacancy relative to the bulk) and three (three coordination vacancies), respectively. We have shown experimentally that methyl dehydrogenation is structure insensitive, showing no significant variation in the activation barrier to dehydrogenation to methylene with changes in cation coordination or local site geometry. Methylene coupling to ethylene is associated with a rate-limiting surface diffusion step on both α-$Cr_2O_3(10\bar{1}\bar{1}2)$ and (0001) surfaces, and shows a significant structure sensitivity. The rate-limiting step shows an 85 K increase in the reaction temperature in TPD on the (0001) due to the lower accessibility of surface O atoms on the stoichiometric (0001) surface. The local

site geometry also requires longer, less-stable bonds as the methylene diffuses across the surface.

For both surfaces, DFT gives an interesting picture of the methylene surface diffusion process. DFT suggests methylene can π-bond to a surface cation, or bridge bond between a surface cation and anion on either surface. The diffusion process is simply a thermally-driven rehybridization in which methylene varies between π-bonded (sp^2) and bridge-bonded (sp^3) configurations, with the barrier to diffusion significantly lower than that for methylene dehydrogenation to surface carbon.

C_1 Reactions on α-Fe_2O_3

Because α-Cr_2O_3 and α-Fe_2O_3 both crystallize in the corundum bulk structure with only minor (less than 2%) differences in the lattice parameters, a comparison of surface chemistry over similar terminations of the two materials allows one to test the impact of a nearly-pure electronic effect associated with the $3d^3$ and $3d^5$ electronic structure of Cr^{3+} and Fe^{3+} cations, respectively. The iron oxide is known to be much more reducible than the chromia, so differences in selectivity due to the reactivity of surface lattice oxygen were anticipated.

Variations in the M^{3+} d-electron density cause dramatic but predictable changes in the surface chemistry of methylene, $:CH_2$, fragments on stoichiometric corundum-structure ($10\bar{1}\bar{1}2$) surfaces when Cr^{3+} cations are replaced with Fe^{3+}. The reaction selectivity on stoichiometric α-Fe_2O_3 ($10\bar{1}\bar{1}2$) is entirely towards the non selective oxidation products CO and CO_2 for small submonolayer doses of the reactant, consistent with the reducible nature of the surface. CO and CO_2 evolve simultaneously (often an indication of a carboxylate surface intermediate) at 630 K in TPD. The reaction of formate formed from the adsorption of formic acid occurs in a similar temperature range to give CO and CO_2, in support of this assignment. No other products are observed from the stoichiometric surface. However, for consecutive TPD runs, the production of CO and CO_2 drop off quickly with the first few doses of reactant, and formaldehyde ($H_2C=O$) and ethylene ($H_2C=CH_2$) appear as major products.

From the products formed, it is clear that methylene fragments reduce the surface via the extraction of lattice oxygen to make CO, CO_2 and $H_2C=O$. The shift in the product slate from nonselective oxidation products (CO, CO_2) to selective oxidation ($H_2C=O$) and $H_2C=CH_2$ occurs as the surface becomes reduced. For methylene coupling to ethylene, the generation of reduced Fe^{2+} surface sites is clearly important, although the specific site requirements (if any) for the coupling reaction are unclear because of a lack of information about the surface structure.

Reactions on Manganese Oxide Surfaces

The increase in d electron density for Fe_2O_3 ($3d^5$ for Fe^{3+} vs $3d^3$ for Cr^{3+}) leads to a highly reducible surface compared to the non-reducible Cr_2O_3. Given the dramatic differences in reaction selectivity observed between these two materials, we have wondered how a $3d^4$ configuration for a Mn^{3+} cation would compare in terms of selectivity. Unfortunately, Mn_2O_3 does not crystallize in the same corundum structure as α-Cr_2O_3 and α-Fe_2O_3, but given that we have found dramatic changes in selectivity associated with electronic changes and primarily kinetic effects from structural changes, we concluded an examination of Mn_2O_3 chemistry would be of interest, regardless of the structural differences. Macroscopic Mn_2O_3 single crystals are not available, but MnO can be purchased from commercial sources. Reports from Langell's group at UNL indicate that the surface of MnO(001) can be oxidized to Mn_2O_3. We have used this approach starting with a MnO(001) single crystal.

We have been able to produce the two higher oxides of manganese via high-temperature oxidation (to Mn_2O_3) and subsequent thermal reduction (to Mn_3O_4). Both higher oxides are disordered, and fail to give a clear diffraction pattern in LEED. Our initial work has focused on water and carbon dioxide adsorption as probe molecules to distinguish differences in the oxides. The higher oxides give very different CO_2 and water TPD signals than ordered $MnO_2(001)$, but the differences for Mn_2O_3 and Mn_3O_4 are minimal.

Since Mn_3O_4 is a mixed valence oxide with both Mn^{2+} and Mn^{3+} cations, we have also tried to produce an ordered Mn^{3+} compound by oxidizing a Na pre-covered MnO surface to produce $NaMnO_2$. The synthesis is fairly straightforward in UHV, but also produces a disordered surface. While our work has failed to produce an ordered Mn^{3+} oxide film that we can characterize structurally, we are currently pursuing a set of TPD reaction studies with C_1 hydrocarbon fragments and oxygenates to test for any obvious differences in selectivity due to the $3d^4$ electronic structure of Mn^{3+} surface cations.

Future Directions

Following the examination of Mn_2O_3 chemistry, we will begin an investigation of mixed valence magnetite (Fe_3O_4) surface chemistry.

Publication list (since 2009) acknowledging the DOE grant or contract

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