

SOLID STATE, SURFACE AND CATALYTIC
STUDIES OF OXIDES

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Research Scope and Objective:

The objective of this research is to elucidate the relationship among the structure, the composition, the chemistry and the catalytic properties of oxide surfaces, and the interrelation between surface and bulk structure and composition. Current emphasis is to study the properties of different crystal faces of ZnO, and of iron oxide of different crystallite sizes and different crystal structures.

Description of Research Effort

Four different crystal surfaces of ZnO, the nonpolar (10 $\bar{1}$ 0), the stepped (40 $\bar{4}$ 1) and (50 $\bar{5}$ 1), and the Zn-polar (0001) surfaces were successfully prepared that possess ordered atomic structure. Their chemical properties were studied by temperature programmed desorption and decomposition (TPD) of CO, CO₂, O₂, methanol, formaldehyde, and formic acid. TPD of CO resulted in the desorption of CO from the stepped and the Zn-polar surfaces, but in the desorption of CO₂ from the stoichiometric nonpolar surface. TPD of CO₂ showed a low temperature peak (\sim 125°C) on the nonpolar and the stepped surface, and a high temperature peak (\sim 410°C) on the Zn-polar surface. TPD of O₂ was similar on all surfaces.

The decomposition of methanol on the nonpolar and the stepped surfaces proceeds via the same mechanism. There are two parallel pathways. In one, surface methoxide, formed by dissociative adsorption of methanol, is hydrogenated to methane. In the other, surface methoxide is oxidized to formate which then decomposes to H₂, CO, CO₂, and H₂O. The decomposition of formaldehyde and formic acid is also via formate. The decomposition of methanol, formaldehyde, and formic acid on the Zn-polar surface also proceeds via the formate intermediate. For methanol, there is the additional pathway of dehydrogenation to formaldehyde and CO. The difference between surfaces can be related to the surface structure. The results indicate that the Zn-polar surface is more metallic in its behavior. Similarity among the desorption of undecomposed species suggests that alcohols and formic acid adsorb associatively on the Zn-polar surface, but dissociatively on the nonpolar surfaces.

Our effort to understand the selectivity for butadiene in butene oxidation

on iron oxide continues. The difference between α - and γ - Fe_2O_3 is now better understood. It was found that one major factor determining butadiene versus CO_2 production in the reaction is the vulnerability to attack by gas phase oxygen of the adsorbed butadiene or its precursor. On α - Fe_2O_3 , this precursor is very sensitive to gas phase oxygen attack. In contrast, it is not sensitive at all on γ - Fe_2O_3 . This difference is also seen as the fact that selectivity is insensitive to the O_2 /butene ratio on γ - Fe_2O_3 , but decreases with increasing O_2 /butene ratio on α - Fe_2O_3 . Another difference, that butadiene desorbs at a lower temperature on γ - than on α - Fe_2O_3 also contributes.

The dependence of the selectivity for butadiene on the crystallite size of α - Fe_2O_3 was investigated over the range of crystallite size from 2.5 nm to >600 nm. The selectivity was high (~80%) for small crystallites and low (<50%) for large crystallites. Extensive characterization of the catalyst samples by X-ray diffraction, X-ray line-shape analysis, Mössbauer spectroscopy, and magnetization measurements confirmed the presence of only α - Fe_2O_3 on the samples studied, except for the smallest size sample which is less well identified. Further work is needed to understand the origin of this phenomenon.

Future Research

Our effort to study the properties of ZnO surfaces will continue. Other stepped surfaces and the O-polar surface will be studied. Characterization by TPD and steady-state reactions will be conducted. Characterization of small Fe_2O_3 crystallites by infrared spectroscopy and other reactions will begin to try to understand the crystallite size effect in oxide catalysis.