

Abstract

Insight into the nature of surfaces and the processes which occur on them is of great importance in the study of catalysis. For example, mixed metal oxides are known to be catalytically active for the oxidation of CO and the reduction of NO_x (automobile exhaust). A practical example of the need for better catalysts is in the chemical industry, where approximately 50% of the total municipal solid waste generated annually is in the form of by-product waste; this amounts to more than 100 million tons annually. The prerequisite of understanding the atomic scale structure at surfaces is what enables the engineering of new and more efficient materials. Through these studies catalytically active sites and reaction pathways may be explored in order to improve the activity and selectivity of catalytic oxidation.

This work focuses on understanding the surface structures of catalytic oxide materials. A low-index face of a model perovskite material, lanthanum aluminate, is investigated through transmission electron diffraction and imaging techniques. The approach taken is to recrystallize the surface through air anneal treatments in an attempt to stabilize different reconstructions. In this study, the discovery of the $(\sqrt{5} \times \sqrt{5})R26.6^\circ$ reconstruction on the LaAlO₃ (001) surface at temperatures between 1100°C - 1500°C is reported. Surface structure analysis is performed with Direct Methods to obtain plausible scattering potential maps, from which the surface unit cell contents can be determined. It is shown that the surface exhibits faceting along the $\langle 100 \rangle$ direction and subsurface voids. Furthermore, an oxygen rich surface containing lanthanum vacancies is shown to be responsible for the surface reconstruction. Density functional theory (DFT) calculations have been performed on the surface, which suggest that an electron hole is localized near the

first one or two surface layers. This charge defect provides the necessary charge balance at the interface. Finally, consequences of the electronic structure redistribution are discussed; as they are likely to be applicable to other oxides and perovskite materials.