

# BERKELEY CATALYSIS CENTER

## Seminar

Friday November 18, 2005

The McCollum Room

775A Tan Hall

2 pm

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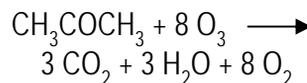
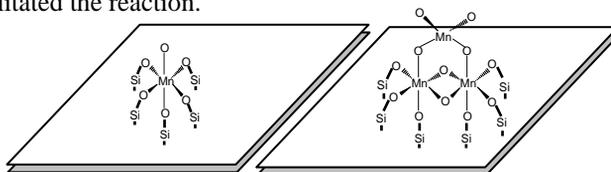
**“True intermediates and spectators in reaction mechanisms:  
A kinetic and spectroscopic study”**

*ABSTRACT:*

An in-depth study of the mechanism of acetone oxidation with ozone was carried out using in situ laser Raman spectroscopy to follow the surface coverages of species derived from the oxidant and the reductant. The catalyst employed was silica-supported manganese oxide (MnO<sub>2</sub>/SiO<sub>2</sub>) because of the well-known activity of manganese oxide as a complete oxidation catalyst. Simultaneous measurements of rate and coverage in transient and steady-state mode allowed determination of the role of the adsorbed species in the reaction.

The work is relevant to the destruction of volatile organic compounds (VOCs), a class of airborne pollutants that are deleterious to human health. Catalytic oxidation using ozone is a promising technology which allows removal of VOCs at low temperatures. Acetone was chosen as the reactant because it is a common industrial solvent, and the health risks associated with acetone are similar to those of many other VOCs.

In order to obtain molecular level information about the various steps in the catalytic reactions, supported catalysts of well-defined structures were used. EXAFS showed that a 3wt % sample had isolated octahedral Mn atoms while a 10wt % sample had clusters resembling fragments of Mn<sub>3</sub>O<sub>4</sub>. The rate was higher on the clusters, indicating that multiple adjacent Mn centers facilitated the reaction.



Two main surface intermediates were identified, a peroxide species derived from ozone, with a band at 890 cm<sup>-1</sup>, and an adsorbed species with intact C-H bonds derived from acetone, with a band at 2930 cm<sup>-1</sup>. Quantitative TPD measurements showed that the peroxide species resides on the manganese and the acetone species is located on the silica support. A mechanism is proposed involving the migration of the adsorbed acetone intermediate from the silica support to the manganese centers where it reacts with atomically adsorbed oxygen species to form complete oxidation products.

Transient experiments, conducted for both acetone and ozone, were used to separately measure the rate of reactant adsorption and the rate of reactant removal (desorption plus reaction) to and from the catalyst surface. By setting the rate of adsorption equal to the rate of removal, steady-state rates for both acetone and ozone reaction as well as coverages for both the acetone and peroxide intermediates were calculated. The coverages obtained through the transient experiments compared favorably to those obtained from in situ Raman spectroscopy measurements under steady-state conditions. However, only the steady-state rate of acetone reaction obtained through the transient experiments compared favorably to the results obtained under steady-state conditions. Thus, the adsorbed peroxide species was determined to be a spectator in the acetone oxidation reaction. The mechanism was proposed to involve the reaction between an adsorbed acetone species and an adsorbed atomic oxygen species to initiate the formation of complete oxidation products.