63b The Mechanism and Kinetics of Methane Oxidation to Formaldehyde over Moox/Sio2

Alexis T. Bell and Nicholas Ohler

The oxidation of methane to formaldehyde were investigated over MoOx/SiO2 with the aim of identifying the mechanism via which this reaction occurs, and in particular the type of oxygen involved in the activation of methane and the size of the oxygen pool. Raman, EXAFS, and XANES characterization demonstrated that the MoOx in the catalyst used is present exclusively as isolated MoO5 species. Reduction of these species occurs such that one O atom per Mo is lost, and this O atom can be replaced upon reoxidation. In situ Raman spectroscopy reveals that the O atom that undergoes redox is that associated with the Mo=O bond. When reoxidation is done with 18O2, only a fraction of the O atoms in the Mo=O bonds are 18O labeled. This observation points to migration of 16O from the support, since no 16O18O is observed in the gas phase. When redox occurs in either a H2/O2 mixture or a CH4/O2 mixture, all of the O atoms in Mo=O are readily exchanged. Isotopic labeling studies done with 18O2 show that the pool of O atoms involved in redox process is large, O/Mo = 15-40. The size of the pool is associated with rapid O scrambling via H2O produced in the redox process. The relationship of these observations to the mechanism and kinetics of methane oxidation to formaldehyde will be discussed.