447c Dft Study of Methane to Acetic Acid Conversion by Pd(II) in Sulfuric Acid

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Any efficient process for converting of methane to acetic acid or methanol will lead to better utilization of natural gas recourses. We have used density functional theory and novel reaction path techniques to map out the reactions involved in the Pd(II)/sulfuric system which converts methane directly to acetic acid. This direct conversion which occurs in 96wt% sulfuric acid at 453 K was reported in 2003 (Periana et al. Science). However the catalytic activity was lost in few hours, presumably because Pd(II) got converted to Pd(0) while oxidizing methane and subsequently precipitated out as Pd black. We used B3LYP theory with LACV3P**++ basis sets and a Poisson-Boltzmann continuum model to calculate energies of optimized structures and transition states in the solution. Transition states were located with the help of a "growing string method" previously developed in our lab (Peters et al. JCP 2004).

Pd(II) exists in the form of 4 coordinated species in sulfuric acid solution. CH4 gets activated to form Pd(II)-CH3 species. This process has an energy barrier of +27.9 kcal/mol. Trace CO that is present in the reaction mixture inserts into the Pd(II)-CH3 bond and forms a Pd(II)-CO-CH3 species. Direct formation of CH3COOH from here will lead to the formation of Pd(0). However such reactions are found to be energetically uphill and have high activation barriers. We found a low barrier pathway which involves the formation of Pd(IV). Sulfuric acid can oxidize Pd(II)-CO-CH3 species to Pd(IV)-CO-CH3 and this Pd(IV) species can desorb CH3COOH while regenerating the Pd(II) species. Based on our thermodynamics calculations we propose that Pd deactivation occurs because Pd(II) gets reduced to Pd(0) by the action of CO.