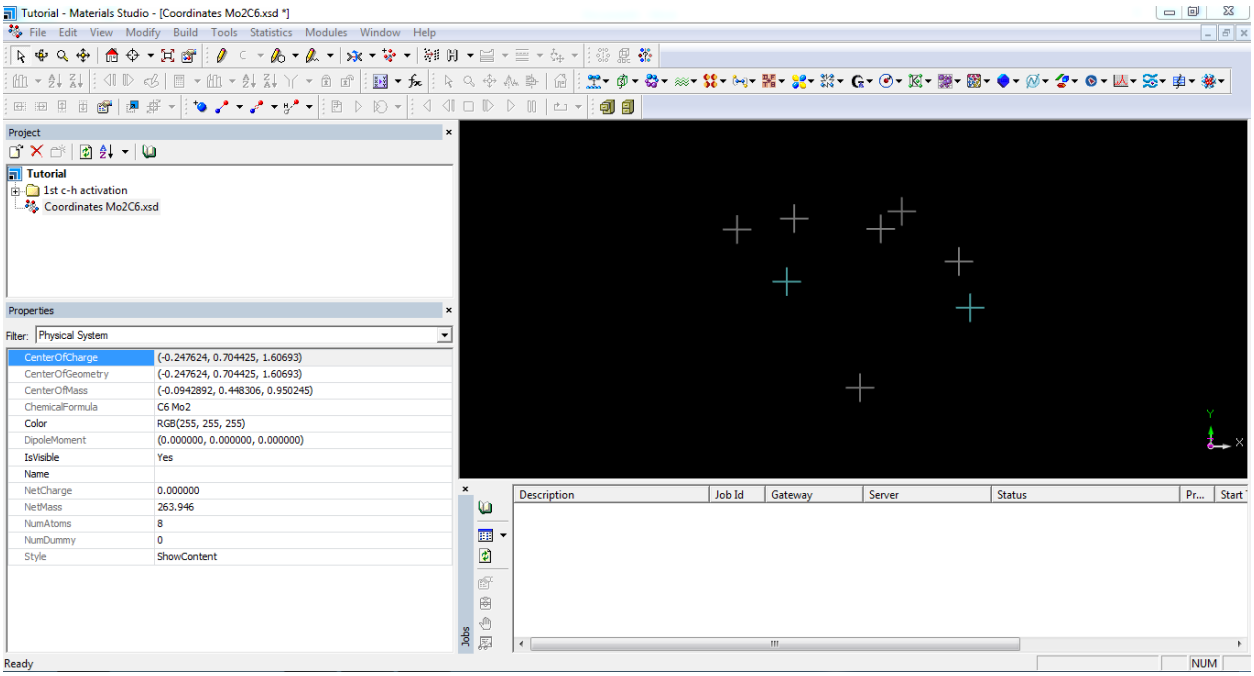
Tutorial on C-H activation on Mo_2C_6 cluster

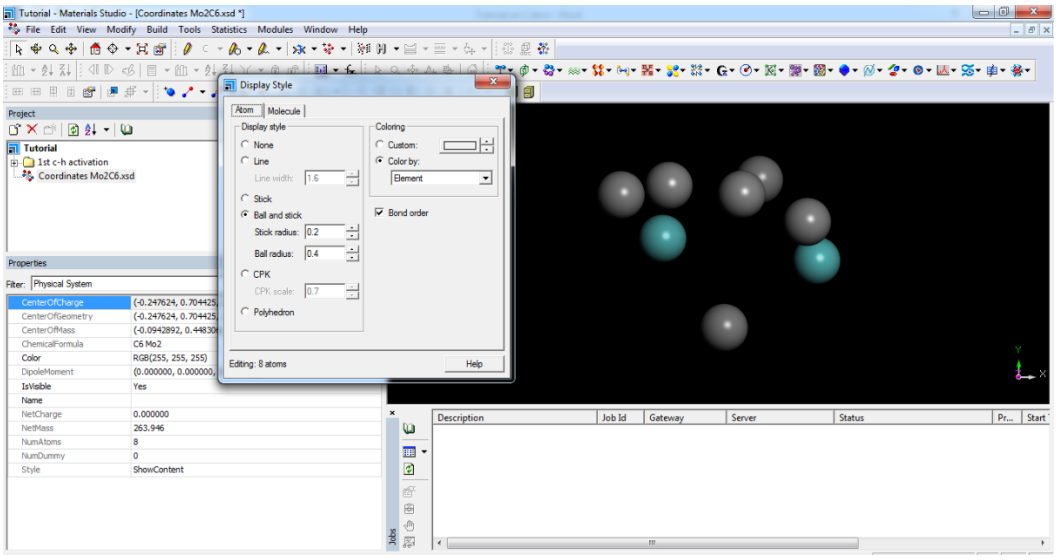
Single step methane conversion under non-oxidative environment to olefin and aromatic compounds over the molybdenum carbide cluster grafted over the shape selective zeolite is promising technology for methane valorization. Being the most stable hydrocarbon, it requires high temperature to active the C-H bond cleavage. This tutorial shows how the methane dehydrogenate over the molybdenum carbide cluster and the energetics required to activate this bond.

Objective: Calculate the activation and reaction energy for methane dehydrogenation over Mo_2C_6 cluster.

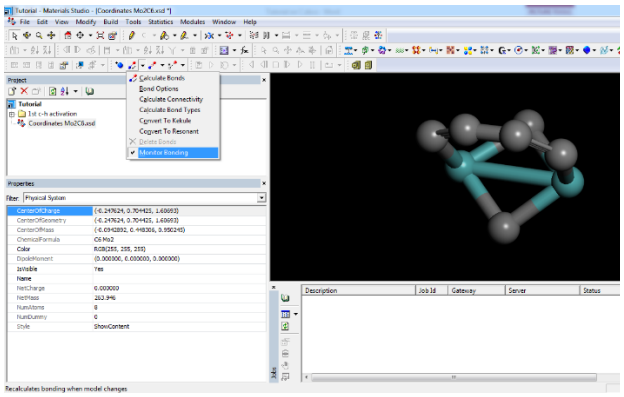
Step 1: Import coordinate file (.xyz) to material studio

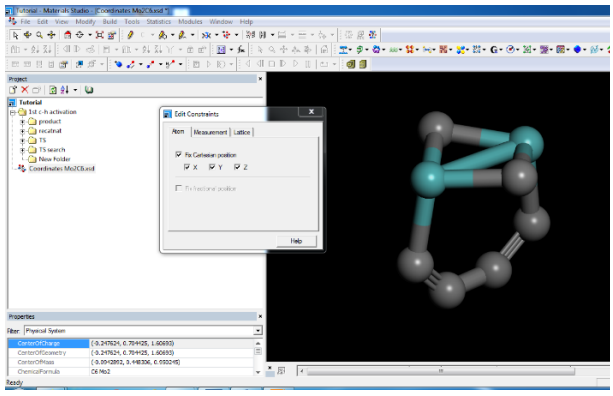


Step 2: Display style

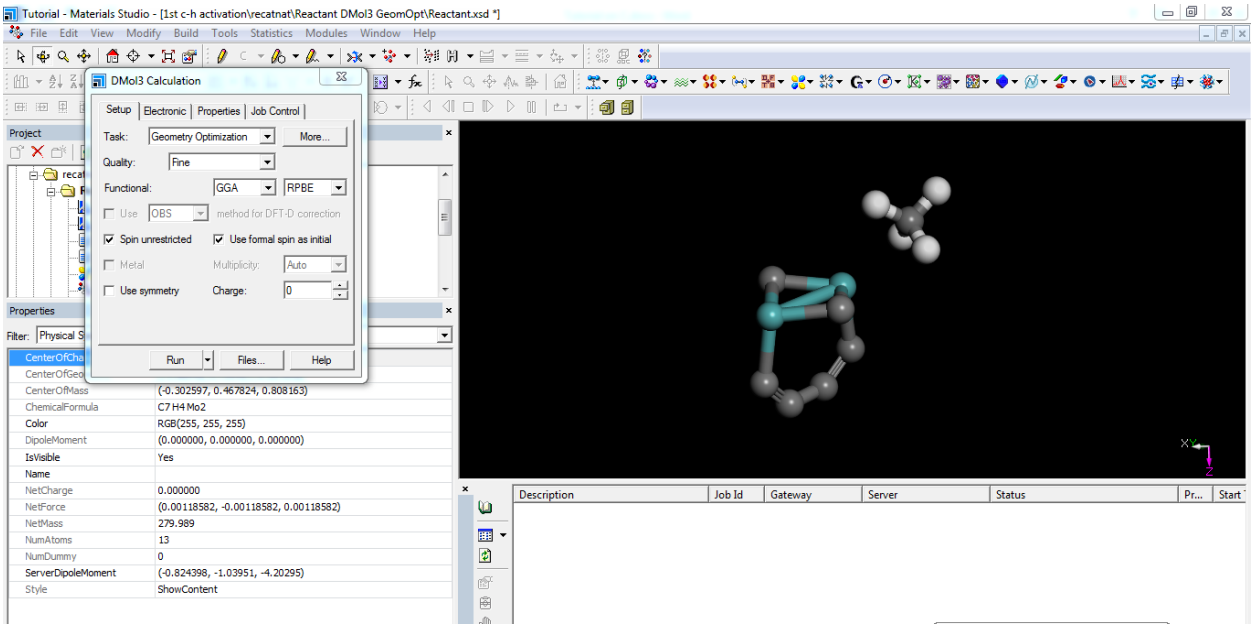


Step 3: Monitor Bonding and Constraint the geometry

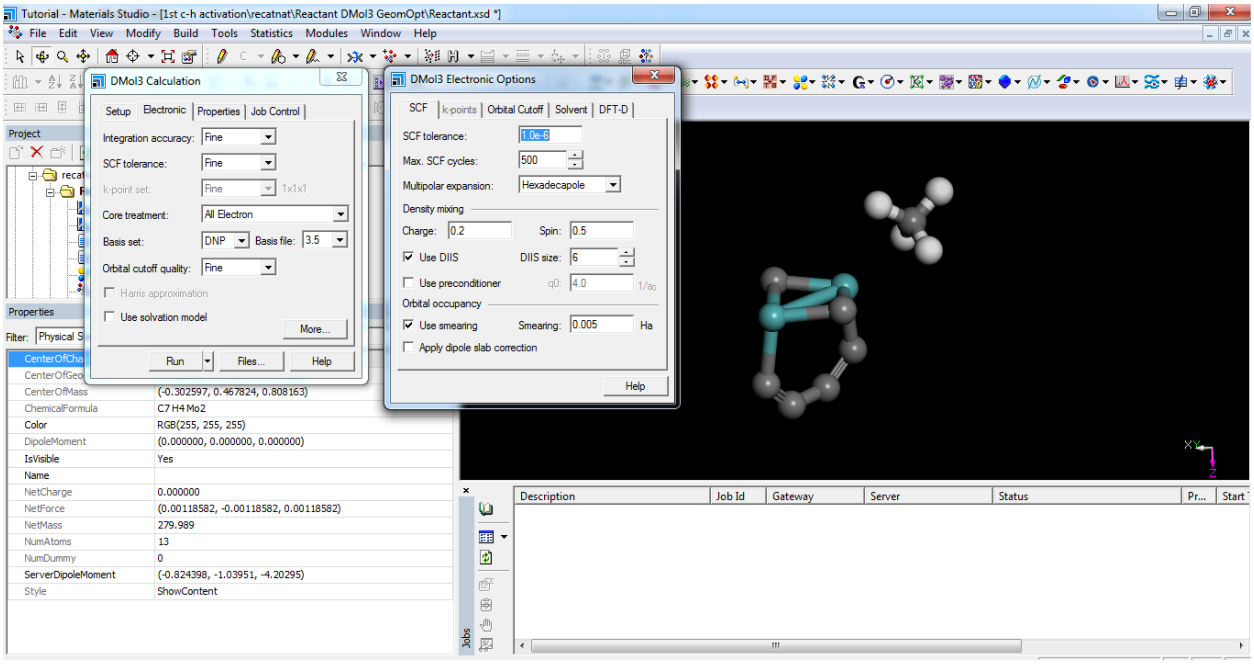




Step 4: Geometry Optimization of Reactant

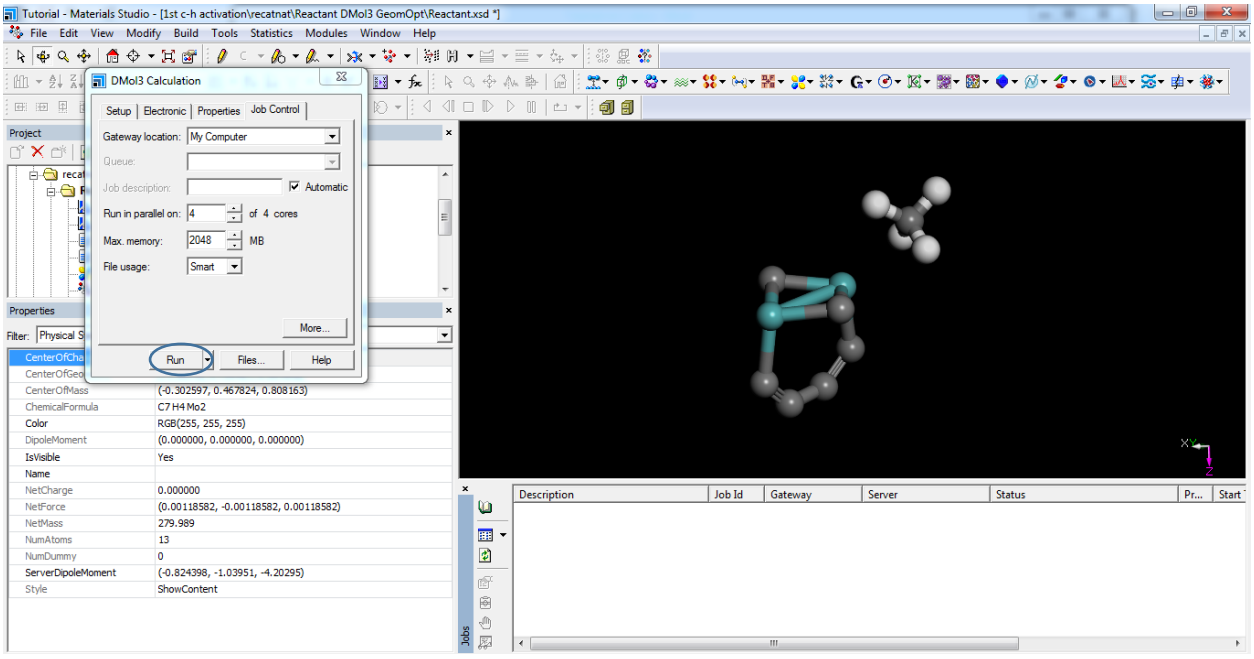


Step 5: Setting up electronic parameters for geometry optimization



Step 6: Setting up property parameters for geometry optimization: Calculate Density of state and Population analysis

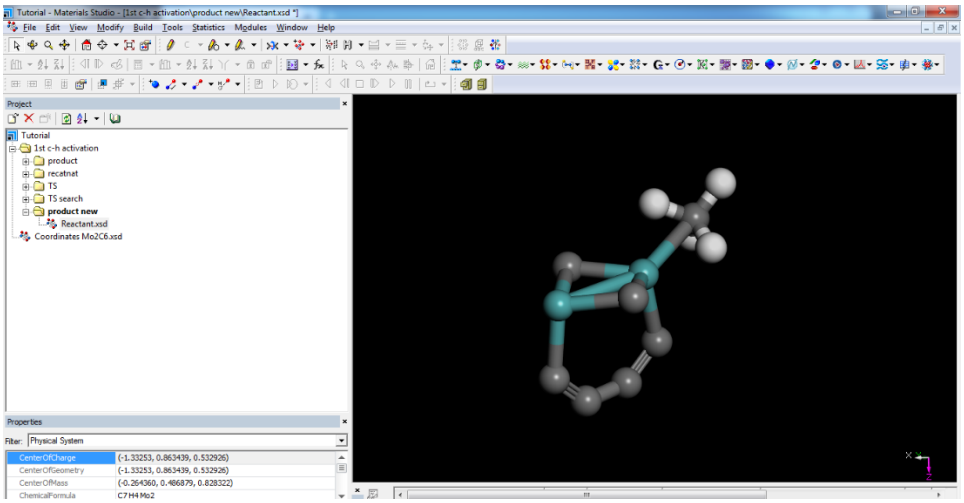
Step 7: Now run the calculation by clicking on run soft key



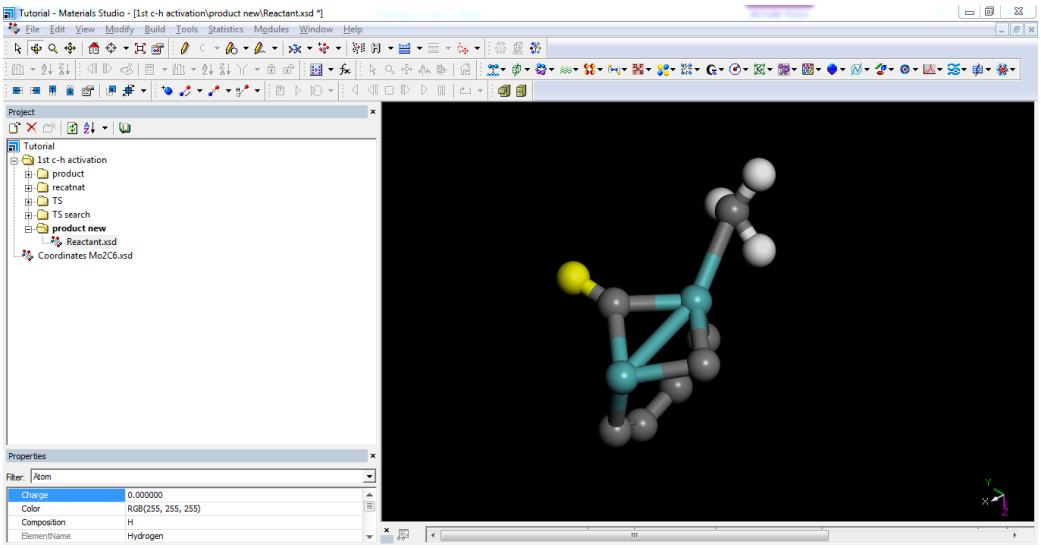
After optimizing reactant, take the same geometry for product optimization and put the parameters same as that used for reactant optimization.

Step 8: Product formation from reactant

Select CH_4 and attach it to Molybdenum through C of CH_4



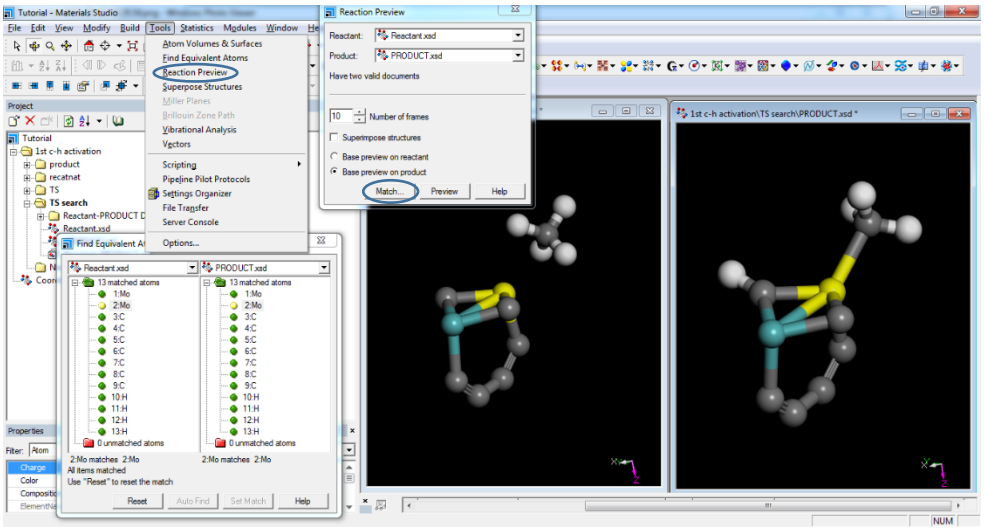
Select H of CH_4 and attach it to "C" of Mo_2C_6



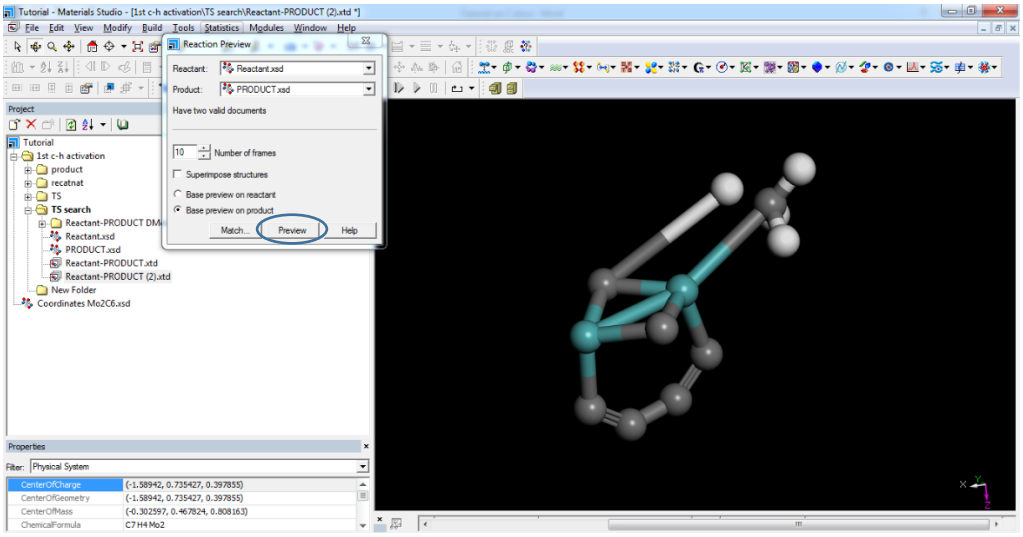
Optimize the product state using geometry optimization tool of DMol3 module.

Step 9: Find transition state for the C-H bond activation

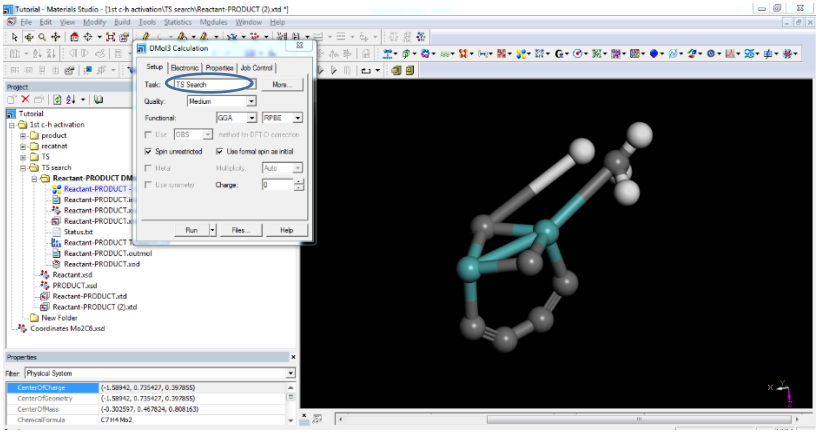
- Make a folder and put optimized reactant and product geometry
- Look for reaction preview and match the atoms of the geometry



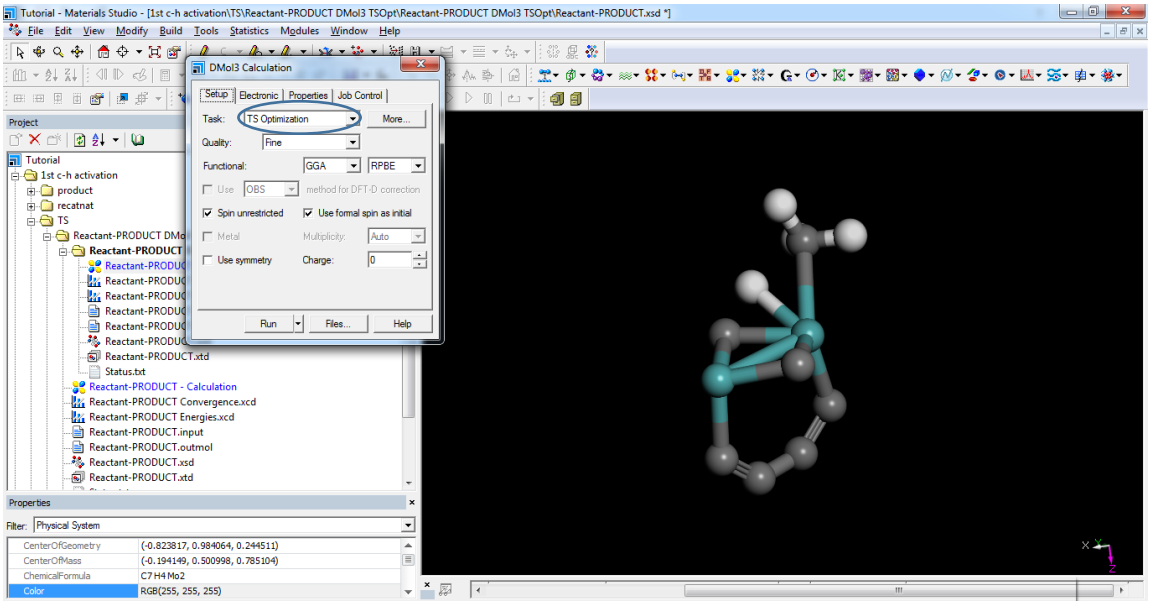
- After matching the atoms, make the reaction preview



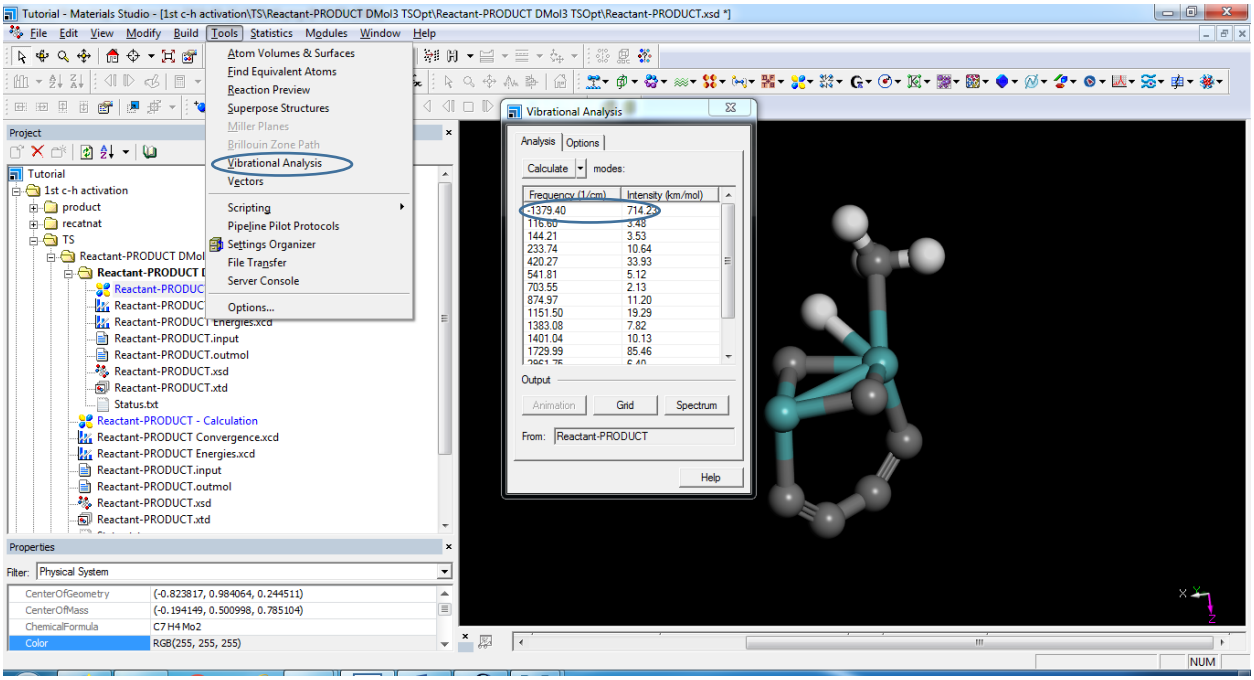
- Transition state search over the obtained TS preview geometry and in properties tab select for frequency to calculate frequency of TS along minimum energy path



Step 10: TS optimization step over the geometry obtained using TS search



- Perform the vibrational analysis over the TS optimization geometry



After successful completion of job we calculate the activation barrier and reaction energy using the energy of the optimized geometries of reactant, product and TS optimization. Activation energy (E_a) is calculated as the difference in the energies between the transition (E_{TS}) and initial states (E_{IS}), $E_a = E_{TS} - E_{IS}$.

The methane activation barrier over the Mo-C site present in the Mo-C-Mo-C plane of the cluster is calculated ~ 130kJ/mol. Plot the reaction energy diagram along with reactant, TS and product geometries corresponding to C-H activation.