Catalytic Effects of Small Pure and Earth-Alkali Mixed Silicon Clusters Sim-nMn (m = 3 – 4, n = 0 – 1) with M = Be, Mg, Ca towards the Methanol Activation

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The methanol activation pathways occurring on small pure and mixed silicon clusters $Si_{m-n}M_n$ with M = Be, Mg, Ca, and m = 3 – 4, n = 0 – 1 were investigated using quantum chemical computations (density functional theory B3LYP/aug-cc-pVTZ and coupled-cluster theory CCSD(T)/CBS extrapolated from energies with the aug-cc-pVnZ basis sets) to examine their thermodynamic and kinetic feasibilities. In all cases considered, the cleavage of the O–H bond is favored over that of the C–H bond. The O–H bond cleavage in the presence of the singlet Si_3 cluster is less thermodynamically preferred than on mixed Si_2M clusters, even though it becomes more kinetically favored. Replacement of one Si atom in the Si_4 cluster with earth-alkaline metals substantially reduces the energy barriers for both O–H and C–H dissociation paths. The most energetically preferred pathway for breaking the O–H bond takes place on the Si_3Ca cluster with a small energy barrier of only 2 kcal/mol. Most importantly, the energy barriers for the O–H bond breaking on the singlet Si_3, Si_2Ca and Si_3Ca clusters are found to be lower than the previously reported results for metal clusters, catalytic metal surfaces, metal oxides…The small mixed Si clusters thus appear to be good catalysts for methanol activation, and most probably in other dehydrogenation processes from the X-H bonds of organic compounds. These findings suggest a further extensive search for doped silicon clusters as realistic catalysts that can experimentally be prepared, for methanol activation particularly and dehydrogenation processes generally.

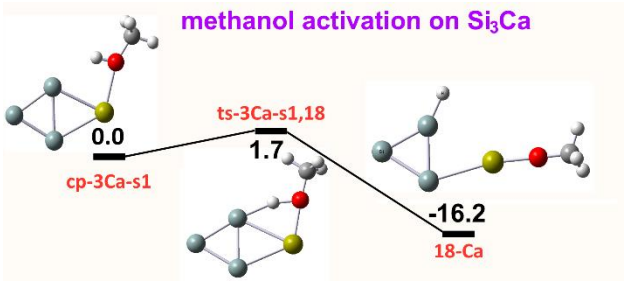

Figure 1: Schematic potential energy profile illustrating the methanol dissociation reaction of methanol in the presence of the singlet Si_3Ca cluster. Relative energies in kcal/mol were obtained from CCSD(T)/CBS + ZPE computations.

[1] Hang, T. D.; Hung, H. M.; Nguyen, H. T.; Nguyen, M. T. Structures, Thermochemical Properties, and Bonding of Mixed Alkaline-Earth-Metal Silicon Trimers $Si_3M^{+/0/-}$ with M = Be, Mg, Ca. *J. Phys. Chem. A* **2015**, *119*, 6493–6503

[2] Hang, T. D, ; Nguyen, H. T. ; Nguyen, M. T. Methanol Activation Catalyzed by Small Earth-Alkali Mixed Silicon Clusters $Si_{m-n}M_n$ with M = Be, Mg, Ca and m = 3 – 4, n = 0 – 1. *J. Phys. Chem. C*, **2016**, *120*, 10442–10451