Cycloaddition of Alkene Molecules on Si(100) Clean Surface

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Chemical modification of Si surfaces has attracted much attention from the viewpoint of engineering such as coating, sensors, molecule-based microelectronics and so on. In particular, cycloaddition of unsaturated organic molecules to a Si(100) clean surface is one of the most important family of chemical reactions, because stable covalent Si-C bonds are formed between each molecule and the surface.

Si(100) clean surface is regularly covered with silicon asymmetric dimers, and partial charge transfer occurs from a down-dimer atom (Sd) to an up-dimer atom (Su) for each dimer. Namely, these Sd and Su sites have ability as Lewis acid and base, respectively, and it is expected that electrophilic and nucleophilic attack will occur at these sites.

We have investigated how these Sd/Su sites on Si(100) surface interact with unsaturated hydrocarbon molecules during the cycloaddition process based on first-principles calculations and experimental results.

First, we briefly review a set of basic concepts for 2+2 cycloaddition reaction of alkene molecules on Si(100) surface and discuss them focusing on atomic configuration and electronic structure of their precursor states [1,2]. These concepts provide us with clear and simple pictures similar to well-known rules in organic chemistry such as Markovnikov's rule. However, actual reaction paths are often affected by temperature and steric hindrance. So next, we theoretically report how these effects appear in case of cycloaddition of 1,4-cyclohexadiene which has been recently revealed to achieve different final adsorption structures depending on its reaction temperature [3].

References
1) M.Nagao, *et al.*, J. Am. Chem. Soc. **126** (2004) 9922.
2) K.Oguchi, *et al.*, J. Am. Chem. Soc. **129** (2007) 1242.
3) private communication with Prof. J. Yoshinobu (ISSP) and Dr. HS. Kato (RIKEN)

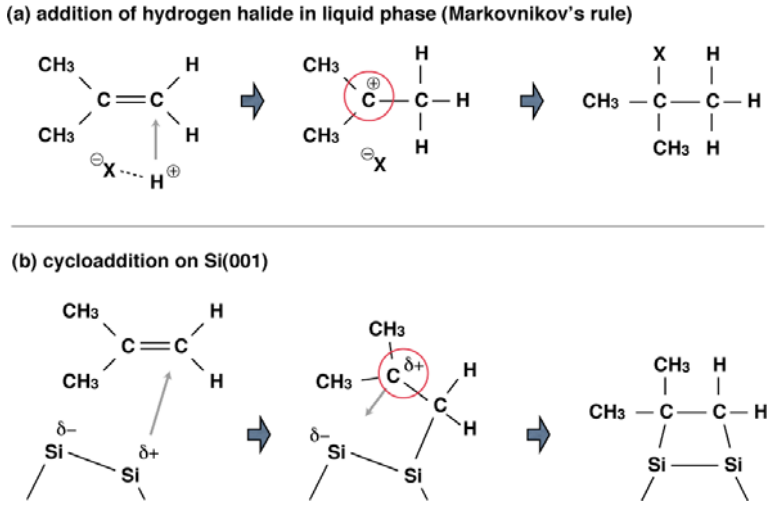

Fig.1 Schematic pictures of reaction mechanisms based on first-principles molecular dynamics calculations. (a) addition of hydrogen halide to 2-methylpropene in liquid phase (an example of Markovnikov's rule). (b) regioselective cycloaddition of 2-methylpropene on Si(100).