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Controlling surface tunneling reactions of solid benzene via surface structure

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Organic molecular solids including thin films and fine particles generally exhibit a range of crystalline phases as well as an amorphous state. The dependence of chemical reactivities on their surface structure has attracted considerable attention because they play a crucial role in an almost limitless amount of research fields, ranging from atmospheric and interstellar chemistry to biological and material sciences. However, despite the rapid accumulation of structural information about organic materials, the correlation between the surface structure of these materials and their chemical properties is not fully understood. Here, we demonstrate that the surface structure of an organic molecular solid determines its chemical reactivity toward an adsorbate. We investigated the following sequential hydrogen (H) atom addition to amorphous and crystalline benzene (C_6H_6)

C_6H_6 + H → C_6H_7 E_a = 18.2 kJ mol^{-1}, [R1]
C_6H_7 + H → C_6H_8, [R2]
C_6H_8 + H → C_6H_9 E_a = 6.3 kJ mol^{-1}, [R3]
C_6H_9 + H → C_6H_{10}, [R4]
C_6H_{10} + H → C_6H_{11} E_a = 10.5 kJ mol^{-1}, [R5]
C_6H_{11} + H → C_6H_{12}. [R6]

E_a is the activation barrier for H-atom addition in the gas phase. The radical recombination reactions R2, R4, and R6 are barrierless on the surface. In situ infrared spectroscopy revealed that cold H atoms can add to the amorphous benzene surface at 20 K to form cyclohexane (C_6H_{12}) by tunneling. However, hydrogenation of crystalline benzene is greatly suppressed. We suggest that the origin of the high selectivity of hydrogenation by tunneling is the difference of geometric constraints; that is, the presence of reactive dangling C_6H_6 molecules that lacks near neighbors on the amorphous C_6H_6 surface and the strong intermolecular steric hindrance on the crystalline C_6H_6. The present findings can lead us to a better understanding of heterogeneous reaction systems involving tunneling, and also provide the possibility of nonenergetic surface chemical modification without undesired side reactions or physical processes.

Keywords: Aromatic hydrocarbons, hydrogenation, amorphous structure, crystalline structure, quantum tunneling, reaction control