Electronic supplementary information:

Preservation of Epoxy Groups on Surfaces in Covalent Attachment of Butadiene Monoxide on Si(111)-(7×7): Effect of Vinyl Substituent

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1. Experimental and computational details

All experiments were carried out in an ultrahigh vacuum (UHV) chamber equipped with an Omicron variable-temperature STM and a HREELS spectrometer (ELS-3000, LK Technologies) at a base pressure below ~2×10^{-10} Torr. A Si(111) wafer (P-doped, R = 1-2 Ω•cm) was cut to a size of 12 mm × 2 mm × 0.5 mm for STM experiments. The Si(111) surface was cleaned by annealing at 1500 K for 10 mins. The cleanliness and surface reconstruction was checked using STM. For HREELS measurements, the size of the sample was 18 mm × 8 mm × 0.5 mm. Two identical Si(111) samples with a Ta-foil sandwiched between them were mounted with two Ta clips, and in turn spot-welded to two Ta rods at the bottom of a Dewar-type sample manipulator. The surface was cleaned by several sputtering-annealing cycles (1 KeV Ar^+ bombardment for 20 mins and followed by annealing at 1200 K for 10 mins). The sample can also be cooled to 110 K using liquid nitrogen. The sample cleanliness was checked by HREELS to ensure that there was no oxide or carbide on the surface.

All the STM data were collected at room temperature (~300 K) and in a constant-current mode with a tunneling current of 0.1 nA. The bias voltage in this study was applied to the sample. HREELS measurements were performed in a specular mode with a primary electron

beam energy of 6.32 eV. The energy resolution for silicon surfaces was ~58 cm^{-1} referring to the full width at half-maximum (FWHM) of the elastic peak.

Butadiene monoxide (Sigmal-Aldrich, 99%) was evaporated into UHV chamber after purification by means of several freeze-pump-thaw cycles to get rid of any dissolved gases. The molecules were introduced into the chamber through a variable leak valve with its aperture about 0.5 m away from the sample surface while keeping the STM scanning on at the same time. For HREELS, the molecular deposition was performed through a dosing tube located at five-centimeters away from the sample surface. After pumping out the residual butadiene monoxide molecules, the sample was transferred to do HREELS measurements. The exposures was measured in Langmuirs (1 Langmuir = 10^{-6} Torr•s).

A cluster model $Si_{16}H_{18}$ (Figure S1) was used to represent an adjacent adatom-rest atom pair. It was cut from the faulted half of an optimized periodic slab of Si(111)-(7×7) and relaxed without any geometric constraints. This model has been successfully used to investigate the dissociative chemisorptions of NH_3[1] and cycloaddition reaction of 1, 3-butadiene[2] on Si(111)-(7×7). All our calculations were performed using the DMol3[3-5] code in Materials Studio. The exchange-correlation potential was set in the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof functional (PBE).[6] The force convergence criterion was set to be 0.02 eV/Å.

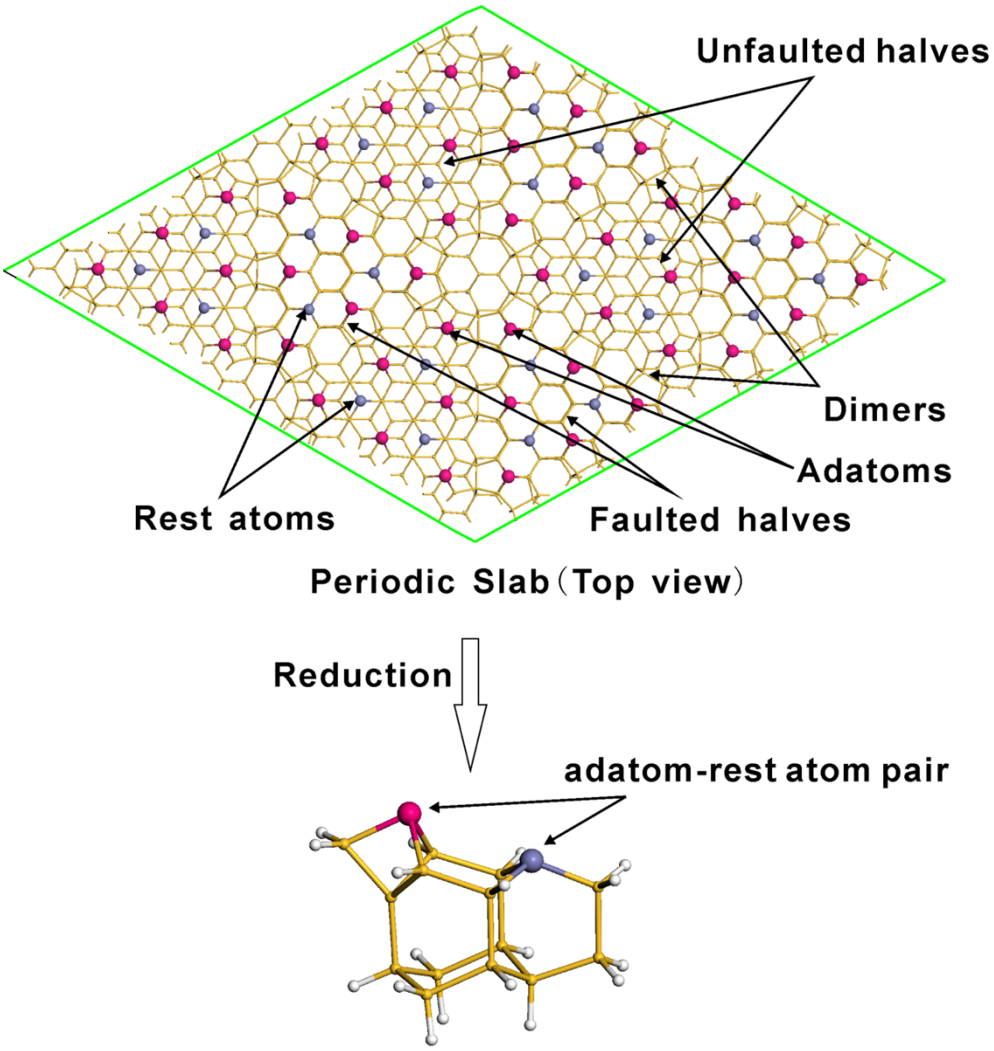

Figure S1: The periodic slab of Si(111)-(7×7) surface contains the five topmost silicon layers surrounding a corner hole. A cluster model $Si_{16}H_{18}$ is cut from the periodic slab to simulate an adjacent adatom-rest atom pair.

Table S1: HREELS vibrational assignments for physisorbed and chemisorbed butadiene monoxide on Si(111)-(7×7).

Vibrational Modes	**HREELS**		**Calculation**		**IR of liquid Butadiene monoxide[8-9]**
	1.5L@110 K	**1.5L@300 K**	**Free molecule**	**[2+2]-like cycloadduct**	
CH_2 asym str (vinyl)	3075	2982	3183	3013	3096
C-H str (vinyl)	2975	2945	3045	2979	2972
C=C str	1634		1642		1651
CH_2 def (vinyl)	1468	1443	1481	1485	1465
CH_2 def (ring)	1418	1410	1396	1403	1443
CH bend (ring)	1318	1310	1366	1383	1347
Ring breathing	1251	1253	1254	1255	1246
CH_2 wag (ring)	1135	1143	1127	1129	1128
CH_2 bend (ring)	1077	1086	1069	1083	1085
CH_2 twist (vinyl)	977	987	983	968	984
CH_2 wag (vinyl)					967
C-C str	935	944	932	959	931
Ring def	819	822	926/850	918/849	921/822
CH_2 rock (ring)	769	761	773	758	778
C-H bend (vinyl)	678	660	651	664	673
Si-C		513		517	

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