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Coverage Dependent Adsorption and Co-adsorption of CO and H_2 on the CdI_2-antitype Metallic $Mo_2C(001)$ Surface

Tao Wang,[a] Xinxin Tian,[b,C] Yong Yang,[b,C] Yong-Wang Li,[b,c] Jianguo Wang,[b] Matthias Beller,[a] Haijun Jiao[a,b,*]

a) Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Strasse 29a, 18059 Rostock, Germany. b) State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, 030001, PR China. c) National Energy Center for Coal to Liquids, Synfuels China Co., Ltd, Huairou District, Beijing, 101400, China

E-mail address: haijun.jiao@catalysis.de

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Table S1. The computed stepwise CO (H_2) adsorption energies without (PBE) and with dispersion corrections (PBE-D2) as well as their differences on the clean CdI_2-antitype (001) surface.

n_{CO}	PBE(E_{ads}/eV)	PBE-D2 (E_{ads}+VDW/eV)	ΔE_{ads}/eV
1CO (1H_2)	-2.08 (-1.61)	-2.33 (-1.79)	-0.25 (-0.18)
2CO (2H_2)	-2.04 (-1.66)	-2.30 (-1.83)	-0.26 (-0.17)
3CO (3H_2)	-2.02 (-1.51)	-2.30 (-1.69)	-0.28 (-0.18)
4CO (4H_2)	-2.00 (-1.48)	-2.27 (-1.65)	-0.28 (-0.17)
5CO (5H_2)	-2.04 (-1.40)	-2.37 (-1.59)	-0.33 (-0.19)
6CO (6H_2)	-2.02 (-1.38)	-2.37 (-1.56)	-0.35 (-0.18)
7CO (7H_2)	-1.89 (-1.33)	-2.26 (-1.53)	-0.37 (-0.20)
8CO (8H_2)	-1.86 (-1.29)	-2.27 (-1.48)	-0.41 (-0.19)
9CO (9H_2)	-1.99 (-0.12)	-2.38 (-0.33)	-0.39 (-0.21)
10CO (10H_2)	-1.92 (-0.22)	-2.33 (-0.43)	-0.41 (-0.21)
11CO (11H_2)	-1.85 (-0.25)	-2.27 (-0.47)	-0.42 (-0.22)
12CO (12H_2)	-1.84 (-0.34)	-2.28 (-0.56)	-0.44 (-0.22)
13CO (13H_2)	-1.60 (-0.19)	-2.04 (-0.40)	-0.45 (-0.21)
14CO (14H_2)	-1.68 (-0.25)	-2.16 (-0.46)	-0.49 (-0.21)
15CO (15H_2)	-1.61 (-0.44)	-2.12 (-0.64)	-0.51 (-0.20)
16CO (16H_2)	-1.54 (-0.46)	-2.08 (-0.67)	-0.54 (-0.21)

Table S2: CO adsorption energies (E_{ads}, eV), C-O distances ($d_{C–O}$, Å) and distances of CO to surface Mo atoms ($d_{Mo–C}$, Å), CO stretching frequency (ν, cm^{-1}) on the CdI_2-antitype $Mo_2C(001)$ surface (**t** for top sites, **b** for bridge sites and **h** for hollow sites)

site	E_{ads}	$d_{C–O}$	$d_{Mo–C}$	$\nu_{C–O}$
$\mathbf{t_1}$	–2.08	1.17	2.03	1942
$\mathbf{b_1}$	–1.56	1.24	1.98, 2.22	1730
$\mathbf{h_1}$	–1.69	1.27	1.98, 2.25, 2.29	1685
$\mathbf{h_2}$	–1.35	1.28	1.97, 2.33, 2.35	1674

Table S3: Vibration frequencies (cm^{-1}) of molecularly adsorbed CO at different coverage on the Mo termination of CdI_2 – antitype - $Mo_2C(001)$ surface.

1CO	1942															
2CO	1944	1937														
3CO	1949	1940	1938													
4CO	1954	1941	1941	1940												
5CO	1980	1947	1945	1942	1932											
6CO	1986	1969	1945	1945	1933	1932										
7CO	2002	1971	1957	1956	1940	1929	1924									
8CO	2007	1985	1955	1954	1954	1953	1923	1920								
9CO	2019	1987	1971	1958	1956	1955	1943	1926	1922							
10CO	2029	1987	1976	1970	1968	1954	1944	1941	1931	1923						
11CO	2040	1992	1983	1980	1973	1964	1949	1944	1943	1932	1924					
12CO	2048	2000	1991	1984	1982	1974	1962	1953	1948	1941	1932	1924				
13CO	2058	2000	1998	1996	1994	1978	1976	1955	1951	1946	1945	1941	1939			
14CO	2064	2003	2002	2000	1999	1991	1984	1959	1958	1955	1951	1949	1948	1940		
15CO	2072	2007	2005	2005	2003	2002	1989	1960	1960	1959	1958	1957	1951	1950	1945	
16CO	2074	2007	2007	2006	2005	2005	2005	1959	1959	1959	1958	1958	1958	1957	1957	1957

Fig. S1: Stable adsorption structures of one CO on the Mo termination of CdI_2-antitype $Mo_2C(001)$ surface (Above for side view, below for top view, blue balls for Mo atoms, red balls for O atoms, gray balls for surface C atoms while black balls for C in CO)

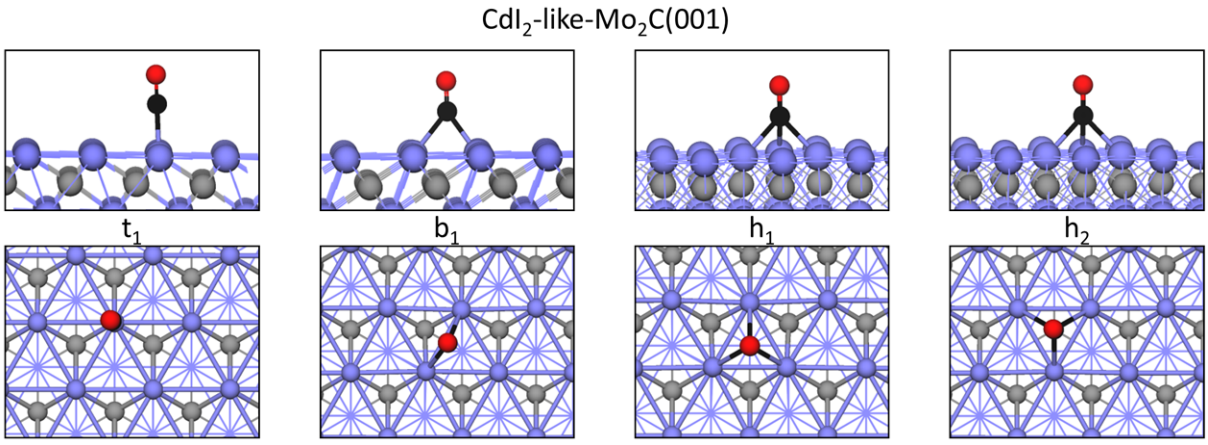

Fig. S2: Dissociative adsorption structures of hydrogen on the clean CdI_2-antitype $Mo_2C(001)$ surface.

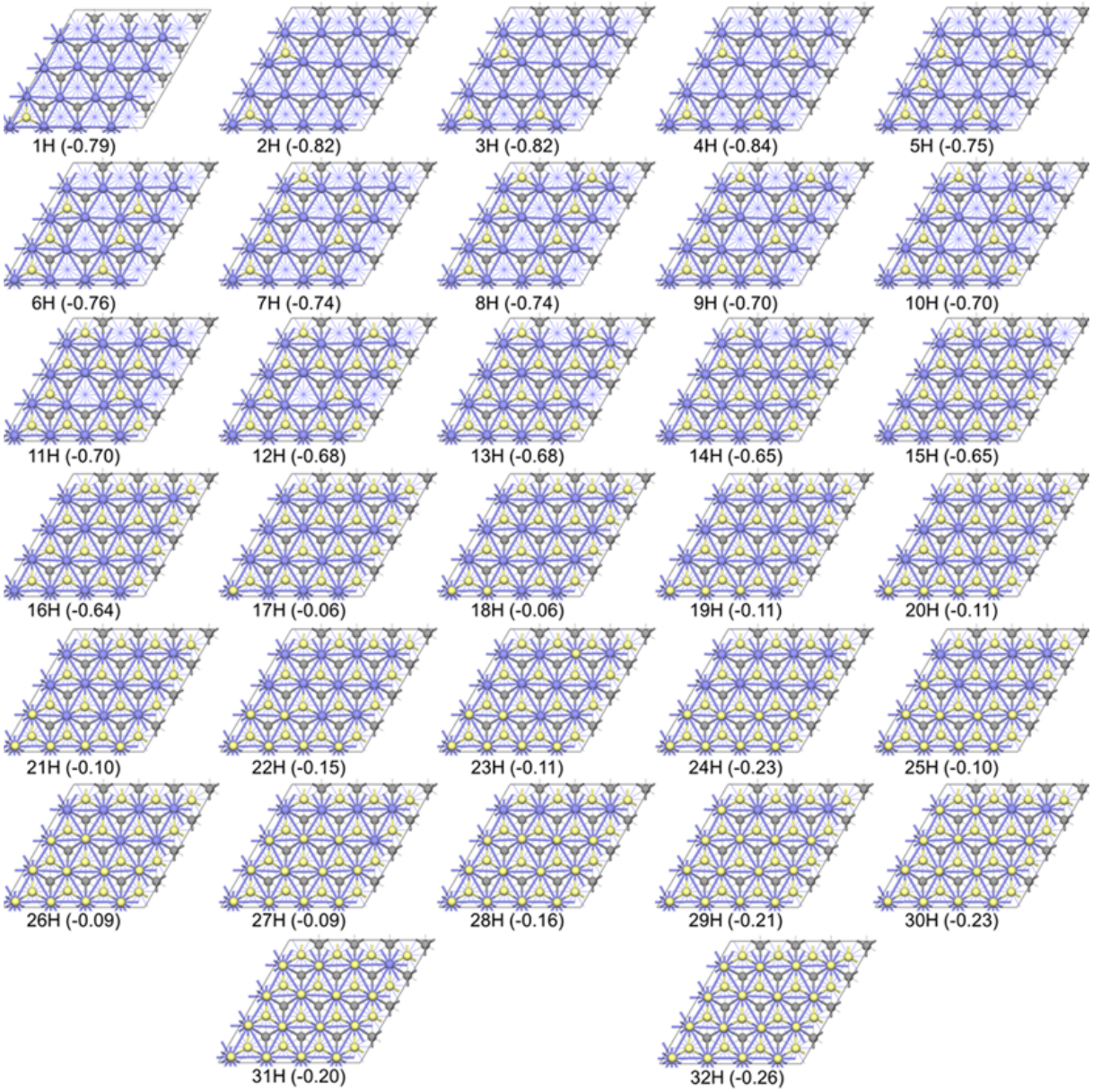

Fig. S3: Dissociative adsorption structures of hydrogen on the 1CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

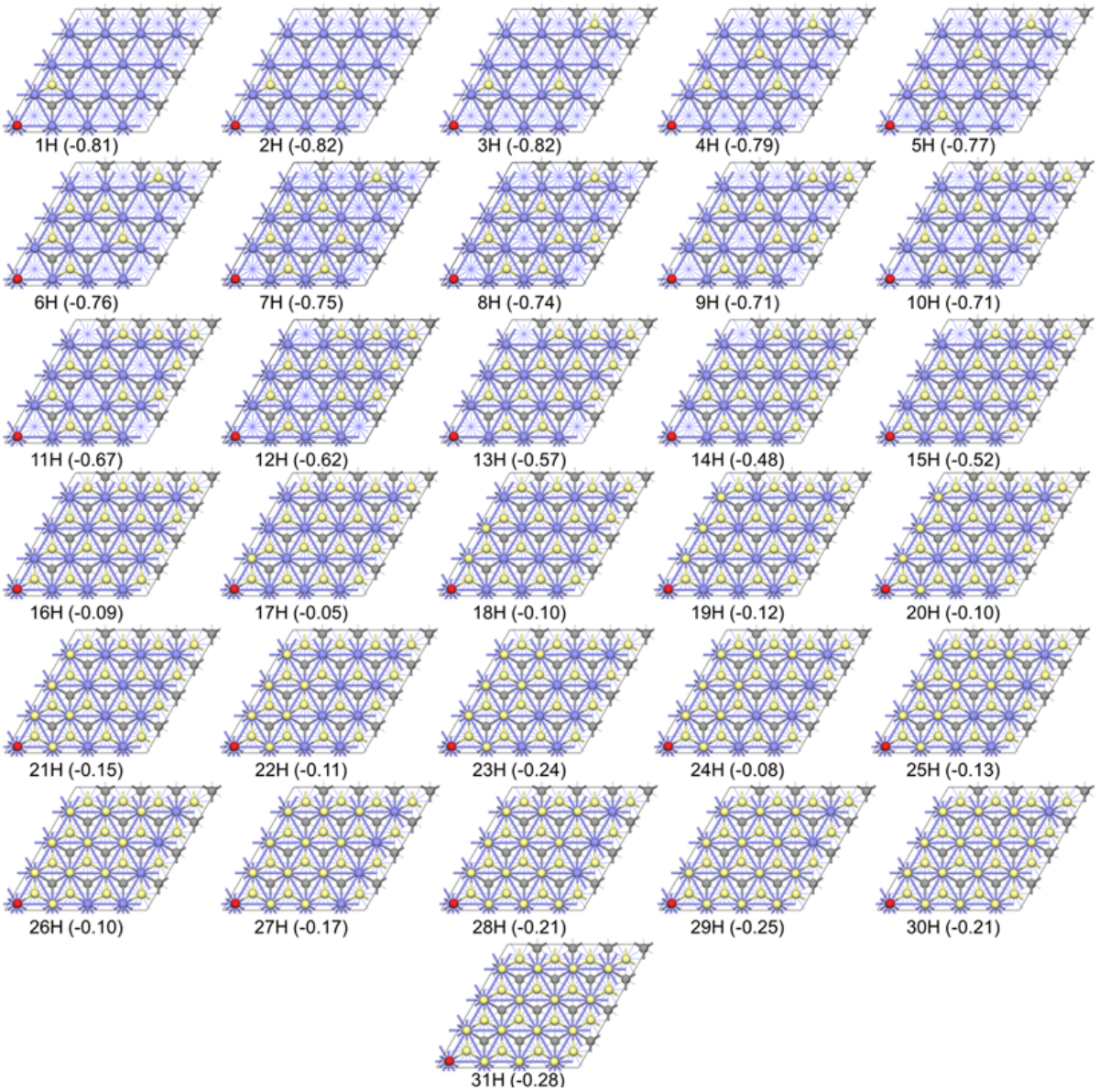

Fig. S4: Dissociative adsorption structures of hydrogen on the 2CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

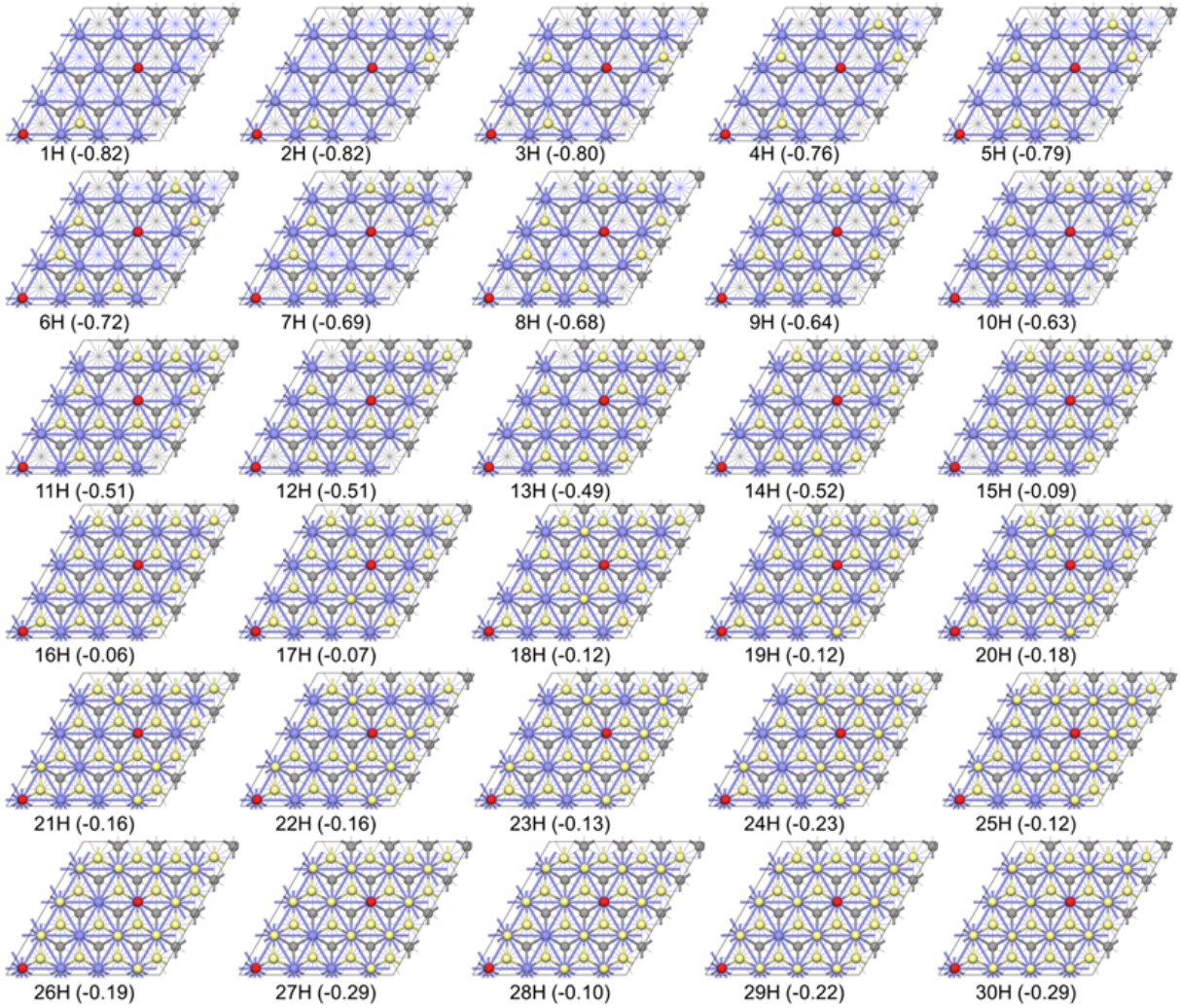

Fig. 5: Dissociative adsorption structures of hydrogen on the 3CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

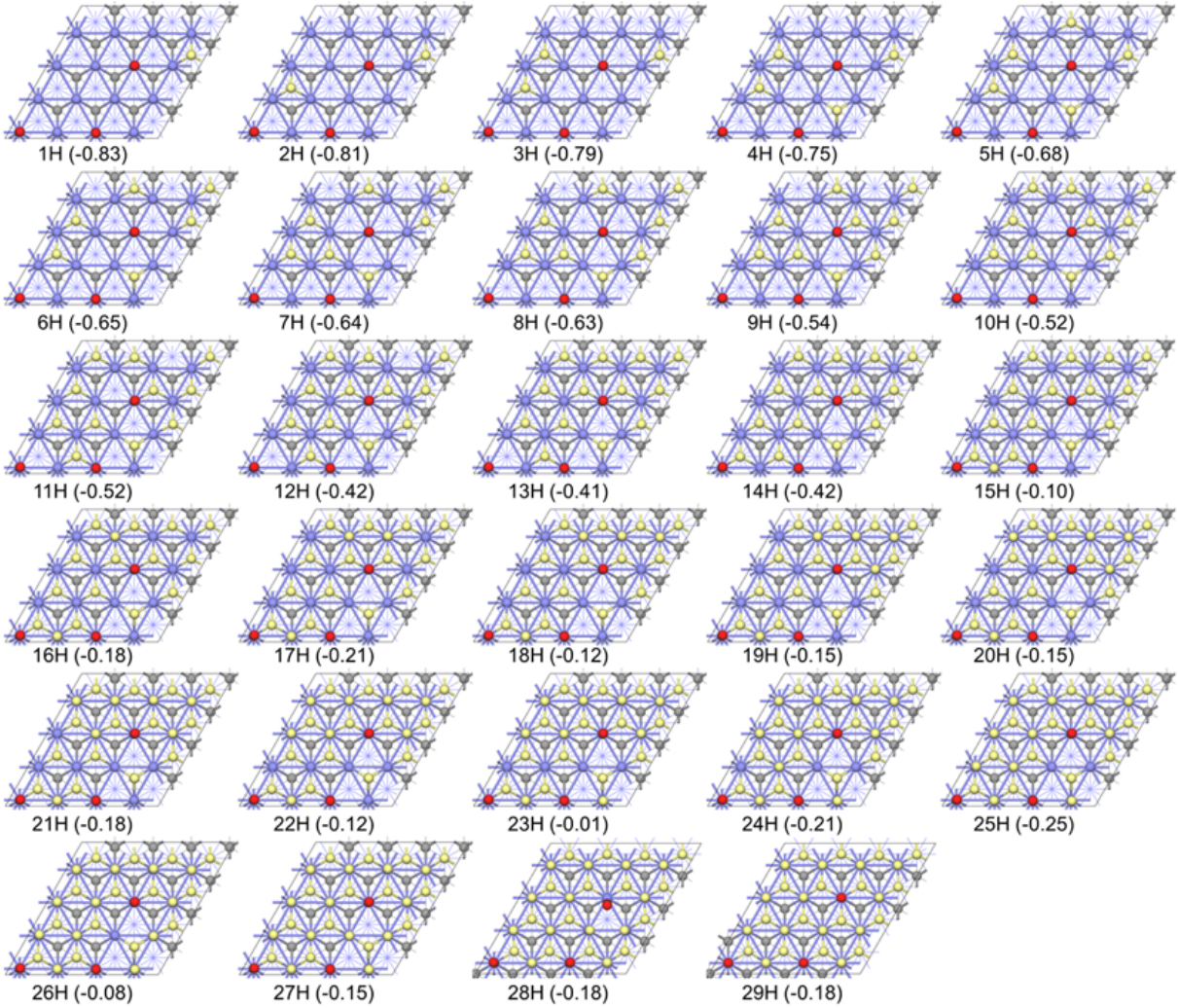

Fig. 6: Dissociative adsorption structures of hydrogen on the 4CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

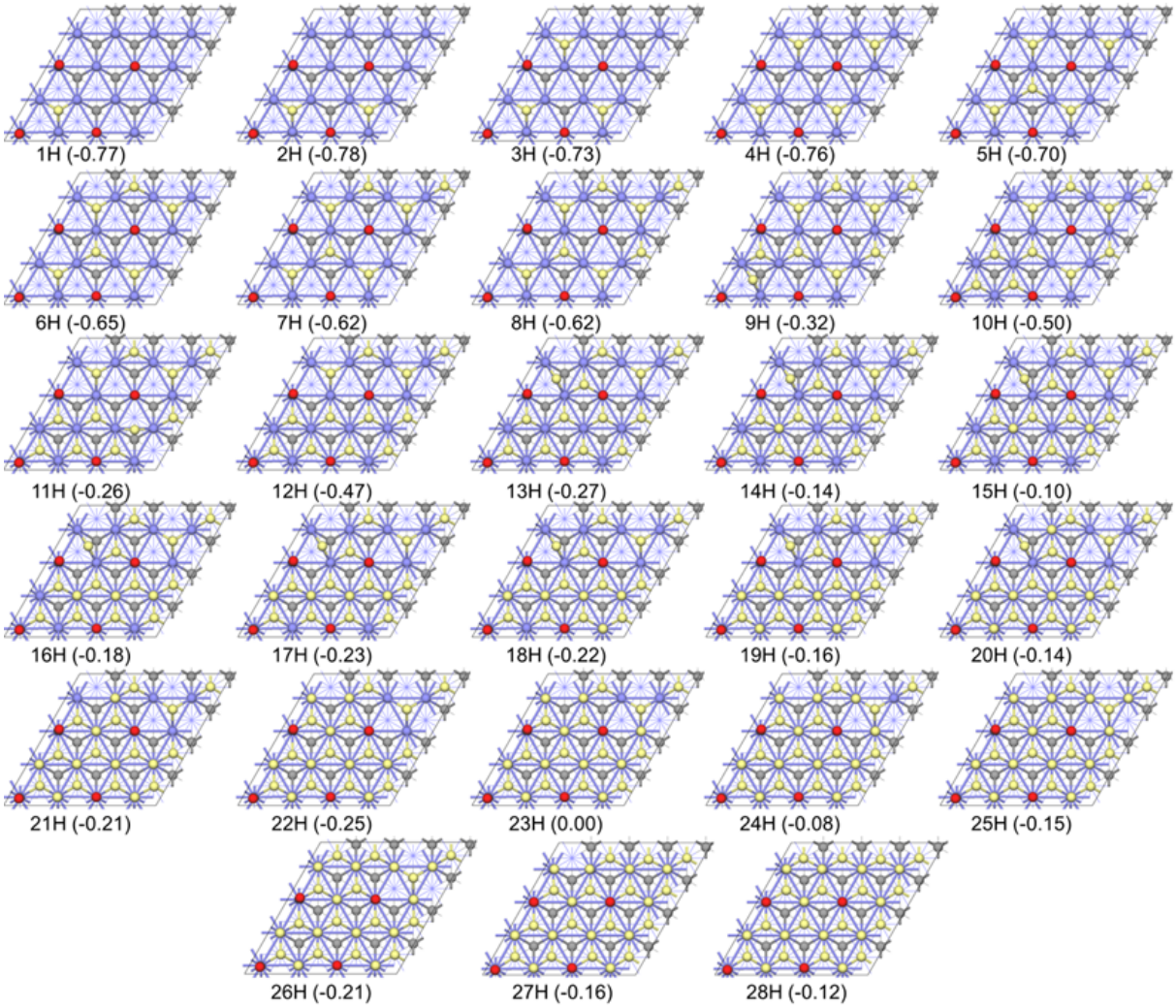

Fig. 7: Dissociative adsorption structures of hydrogen on the 5CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

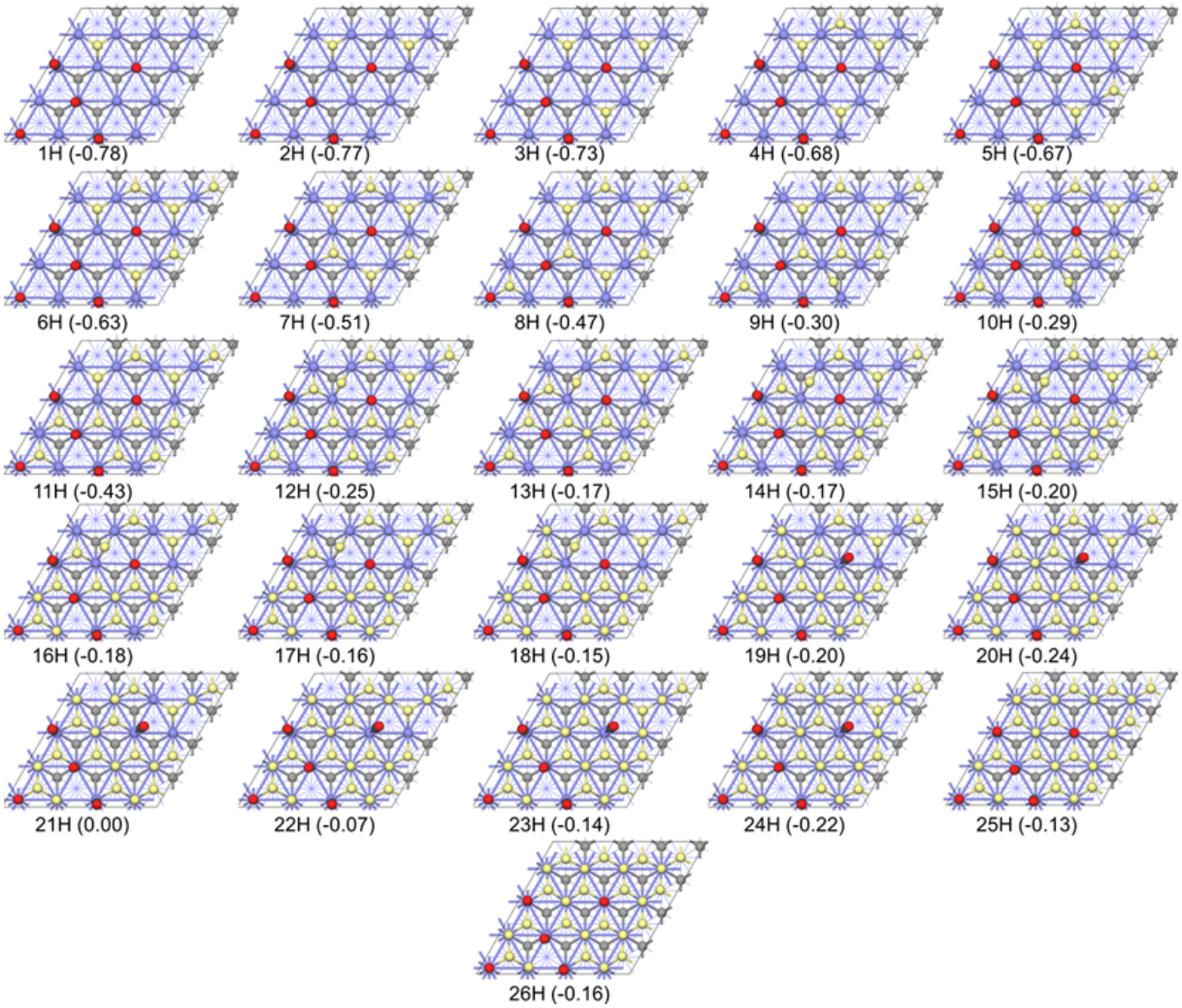

Fig. 8: Dissociative adsorption structures of hydrogen on the 6CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

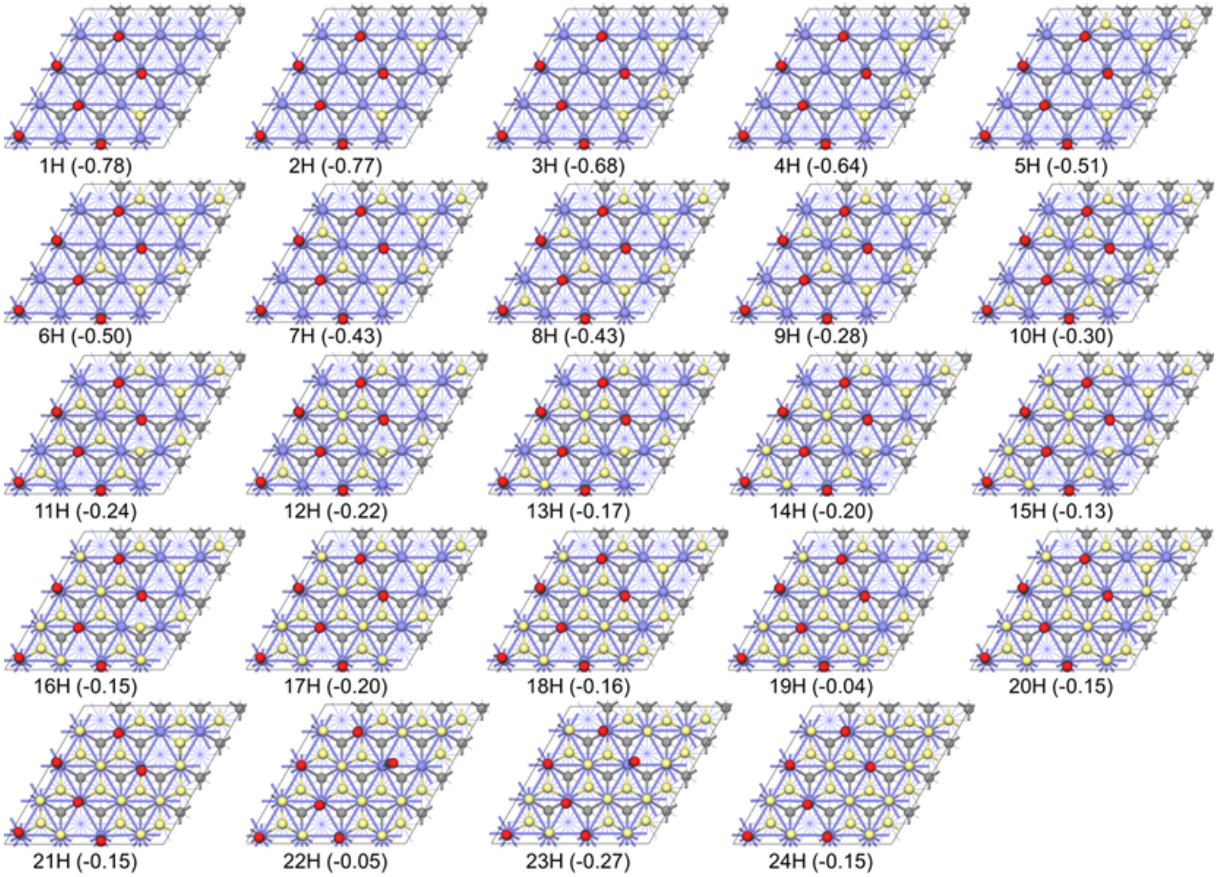

Fig. 9: Dissociative adsorption structures of hydrogen on the 7CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

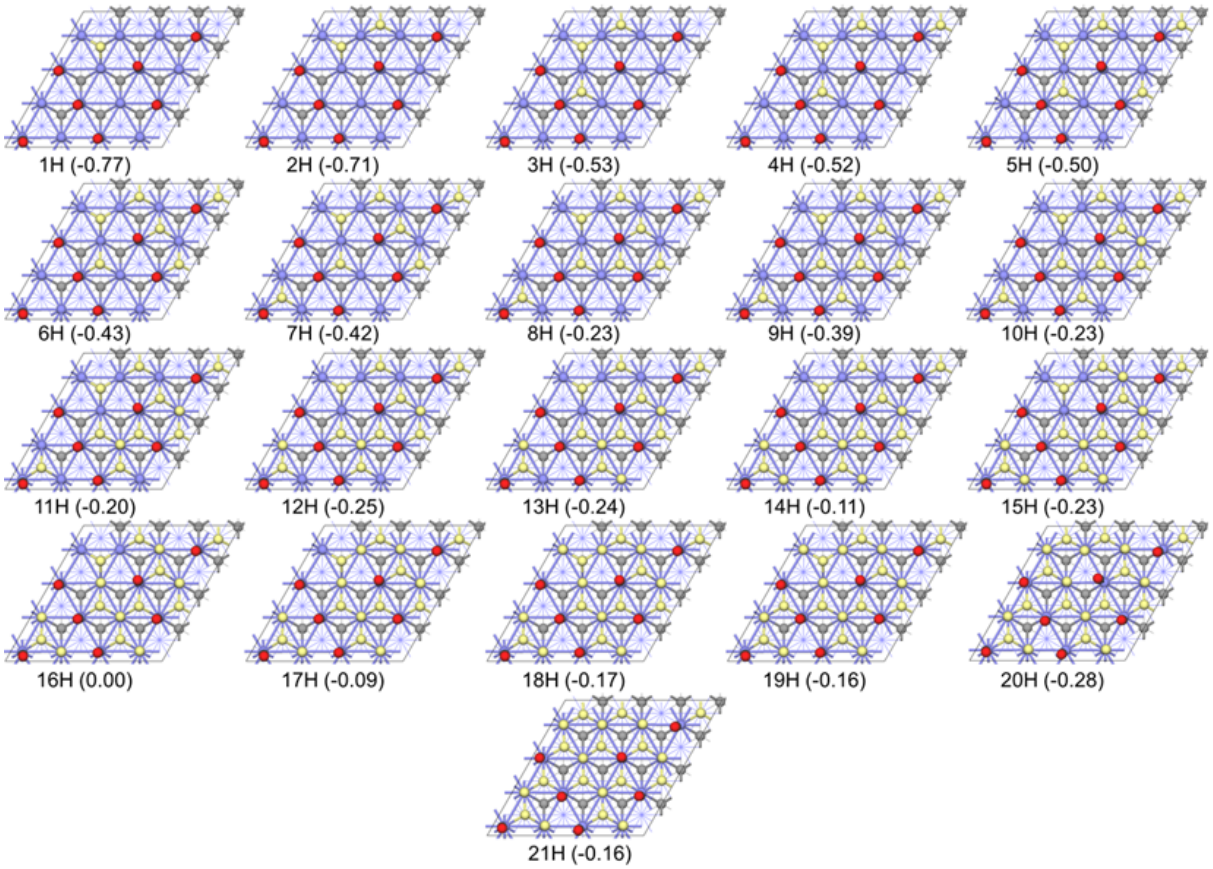

Fig. 10: Dissociative adsorption structures of hydrogen on the 8CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

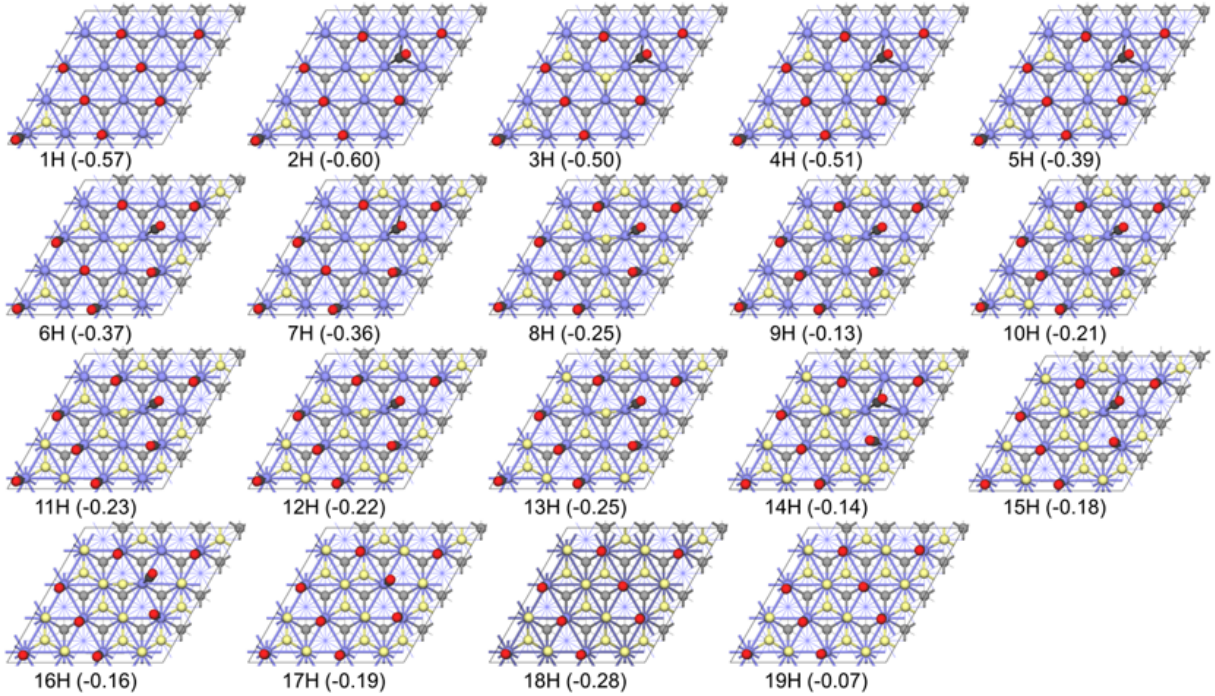

Fig. 11: Dissociative adsorption structures of hydrogen on the 9CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

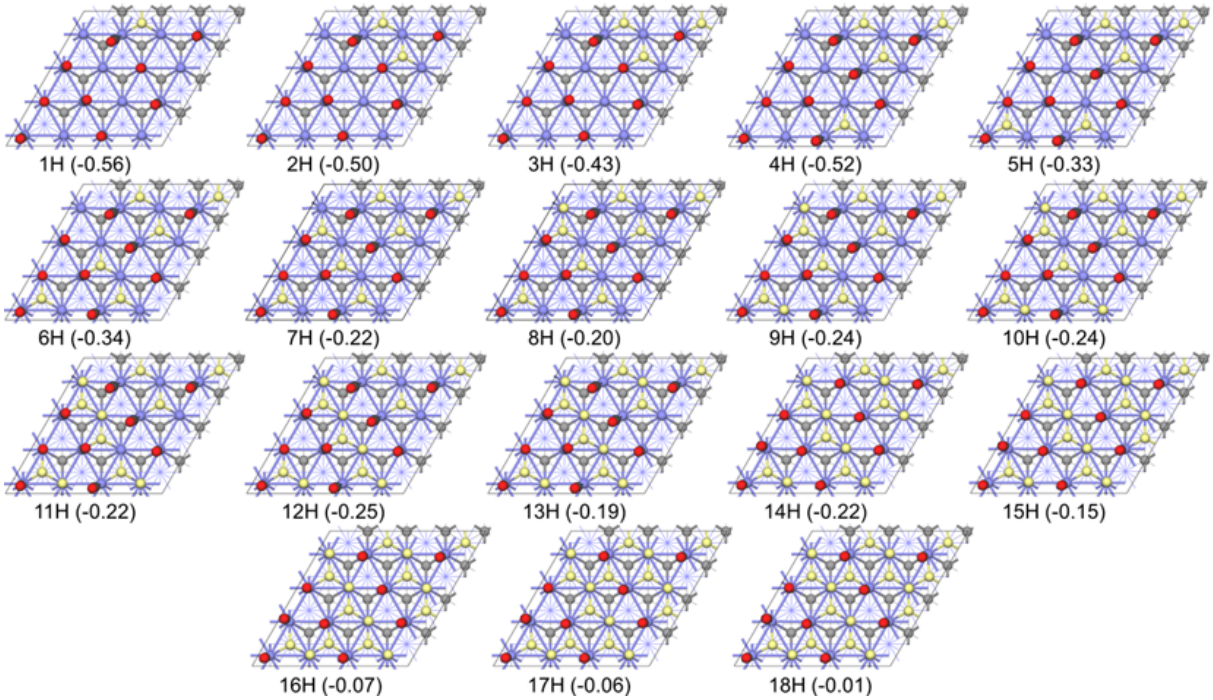

Fig. 12: Dissociative adsorption structures of hydrogen on the 10CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

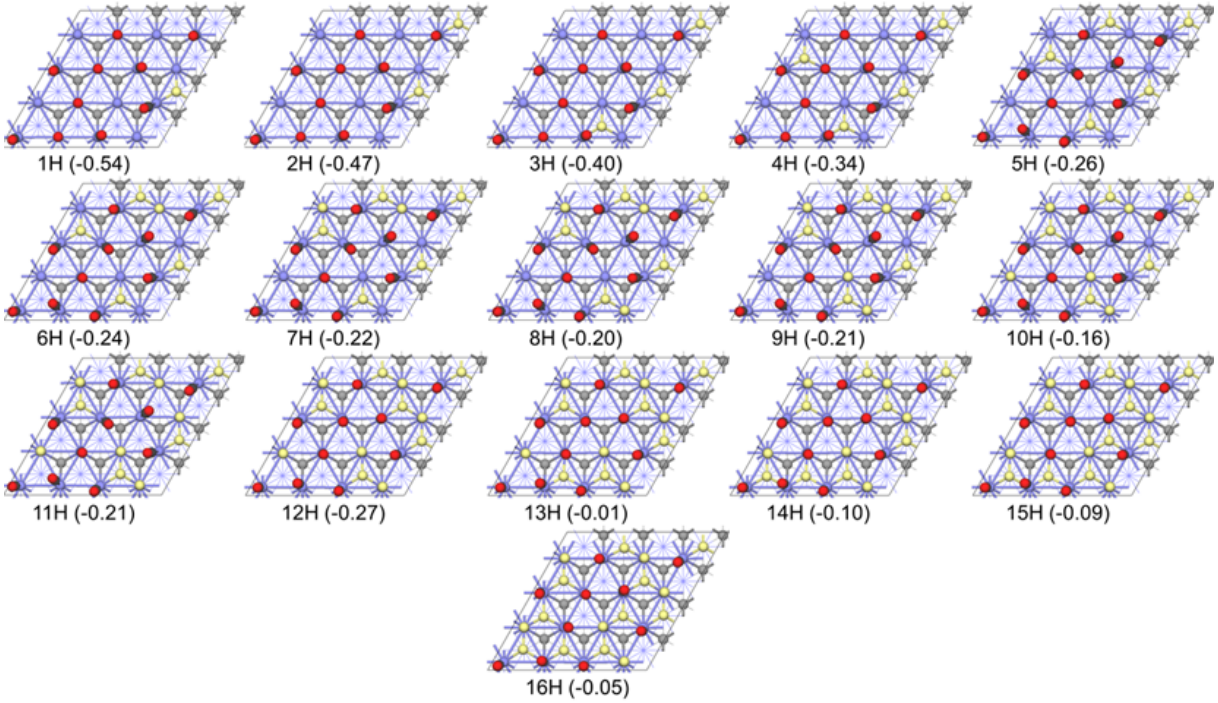

Fig. 13: Dissociative adsorption structures of hydrogen on the 11CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

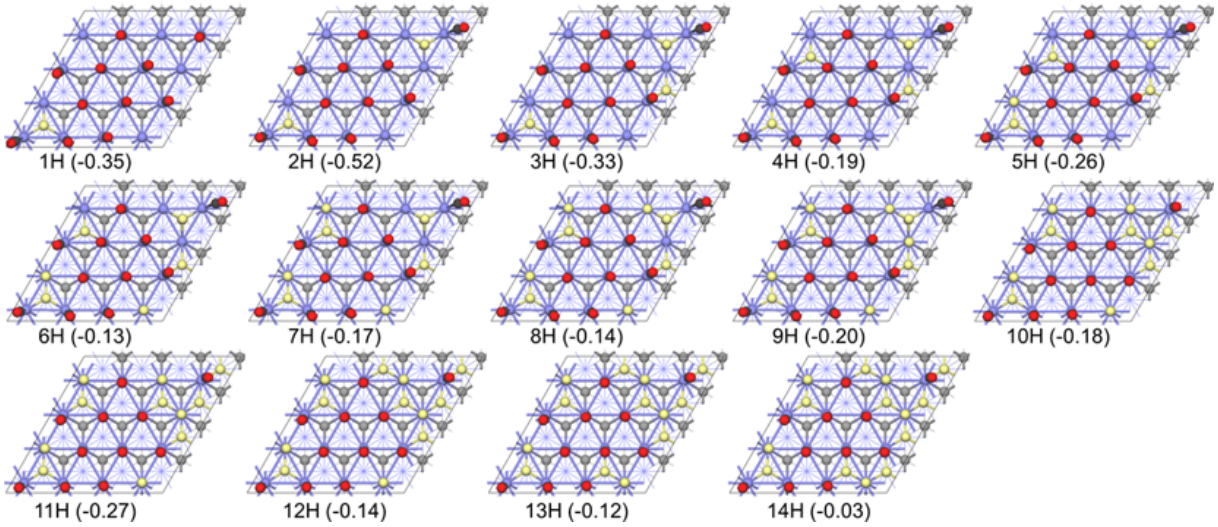

Fig. 14: Dissociative adsorption structures of hydrogen on the 12CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

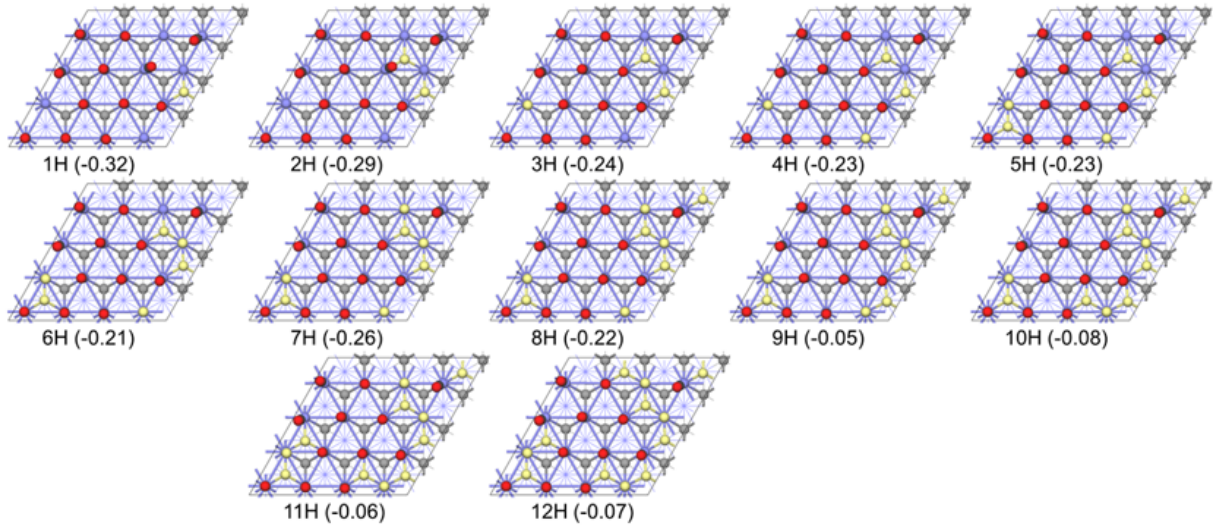

Fig. 15: Dissociative adsorption structures of hydrogen on the 13CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

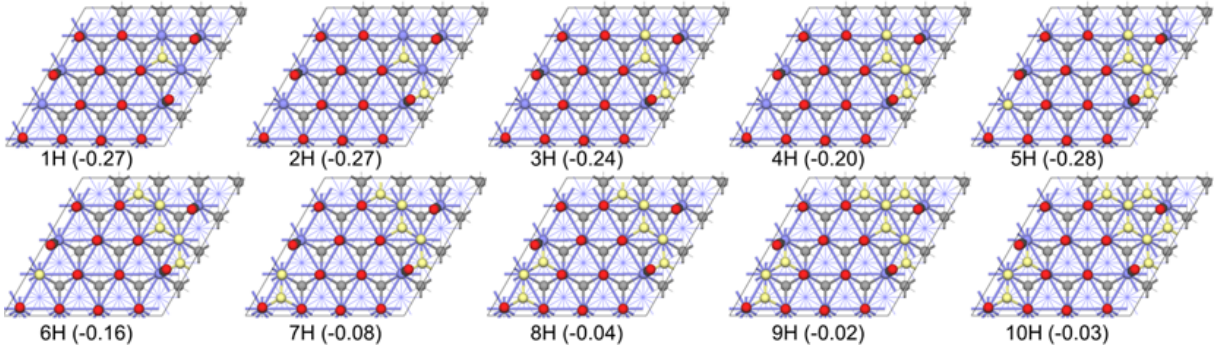

Fig. 16: Dissociative adsorption structures of hydrogen on the 14CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

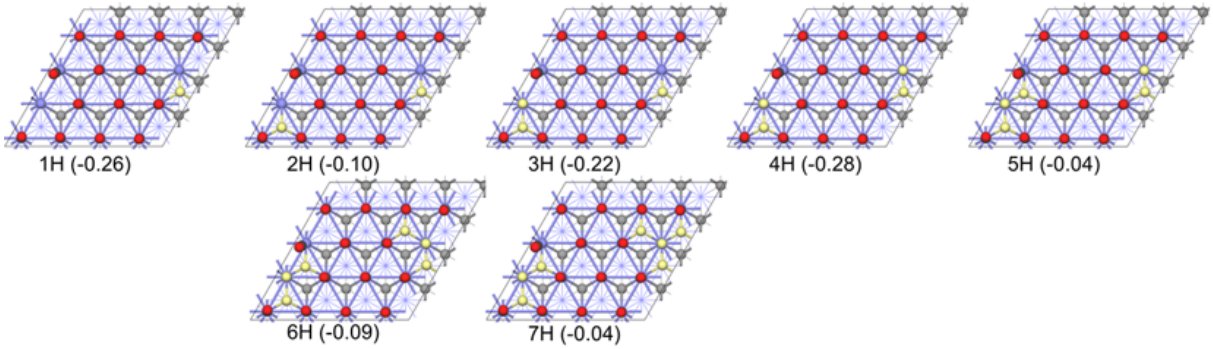

Fig. 17: Dissociative adsorption structures of hydrogen on the 15CO pre-covered CdI_2-antitype $Mo_2C(001)$ surface.

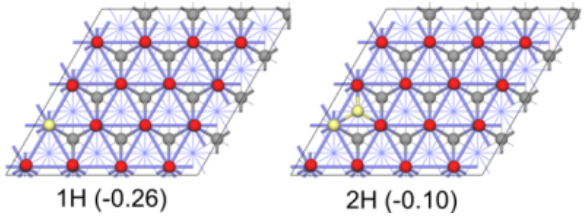

Fig. S18: Schematic structures of the Mo termination of CdI_2-antitype-Mo_2C(001) surface (a), Eclipse-Mo_2C(001) surface (b) and Orthorhombic-Mo_2C(100) surface(c) as well as possible adsorption sites (Blue balls for Mo atoms, gray balls for first layer C atoms and black balls for C atoms in other layers, t for top, b for bridge and h for hollow)

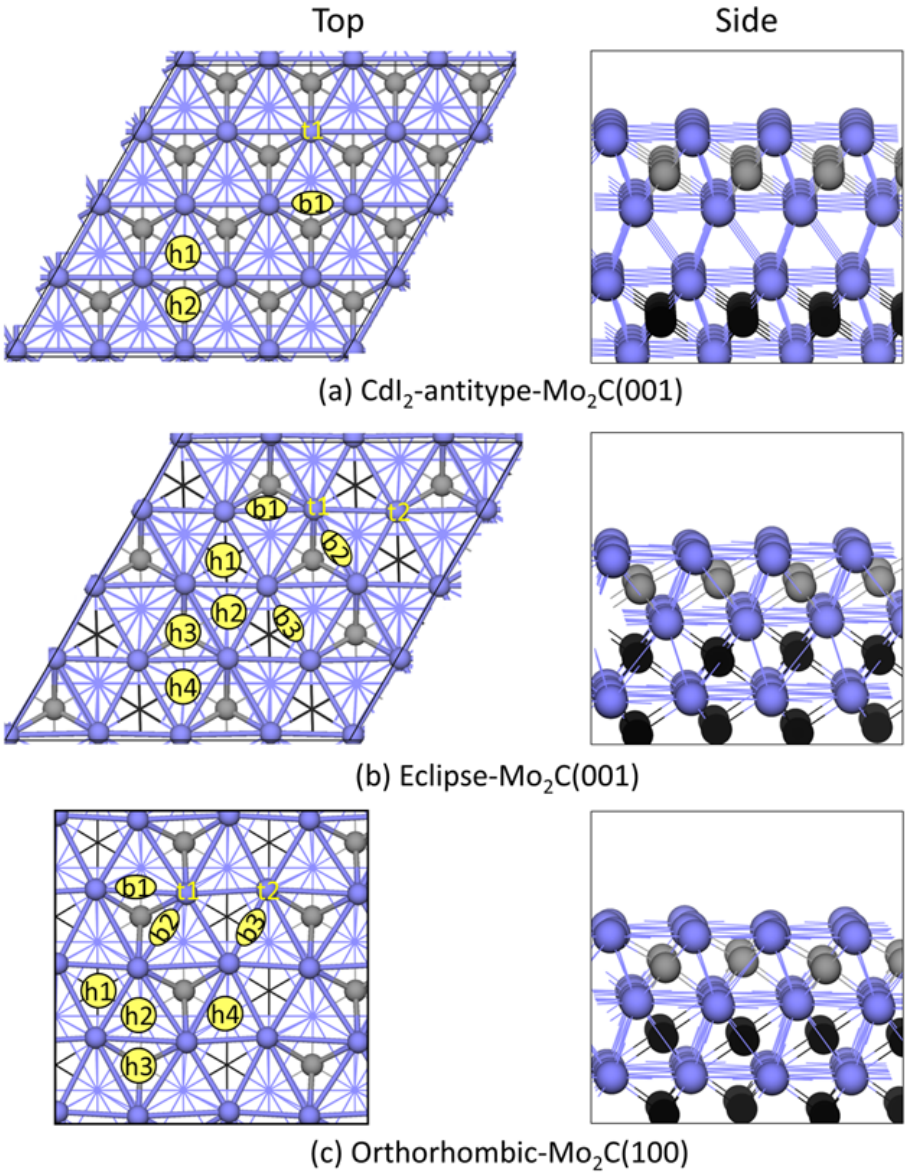

Fig. S19: Density of the CdI_2-antitype-Mo_2C(001), eclipsed-Mo_2C(001) and orthorhombic-Mo_2C(100) surfaces