

Electronic Supplementary Information

Decomposition mechanism of methylamine to hydrogen cyanide on Pt(111): Selectivity of the C–H, N–H and C–N bond scissions

Zhigang Deng, Xiaoqing Lu*, Zengqiang Wen, Shuxian Wei, Qing Zhu, Dongliang
Jin, Xiaofan Shi, Wenyue Guo*

College of Science, China University of Petroleum, Qingdao, Shandong 266580, P. R.

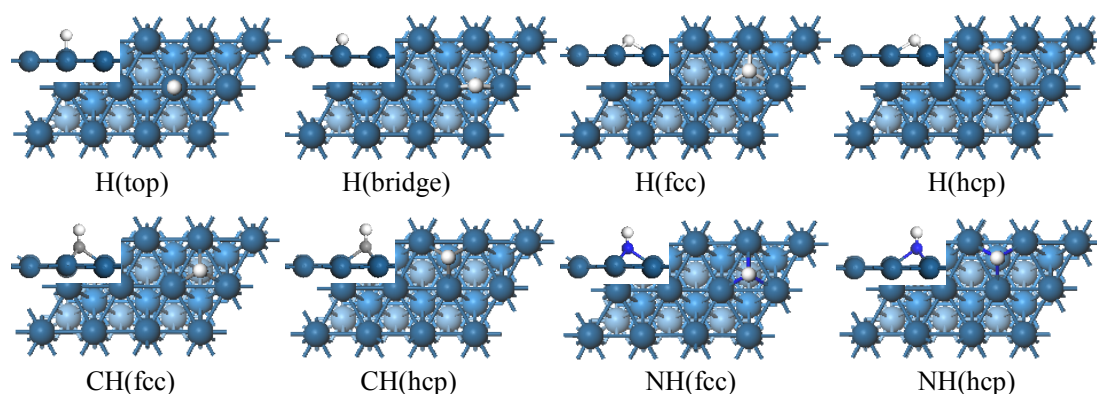
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*Corresponding authors: Xiaoqing Lu, Wenyue Guo

E-mail address: luxq@upc.edu.cn and wyguo@upc.edu.cn

Telephone: 86-532-8698-1334; Fax numbers: 86-532-8698-3363

Fig. S1 The stable adsorption configurations of H, CH and NH on (2×3) cell Pt(111).

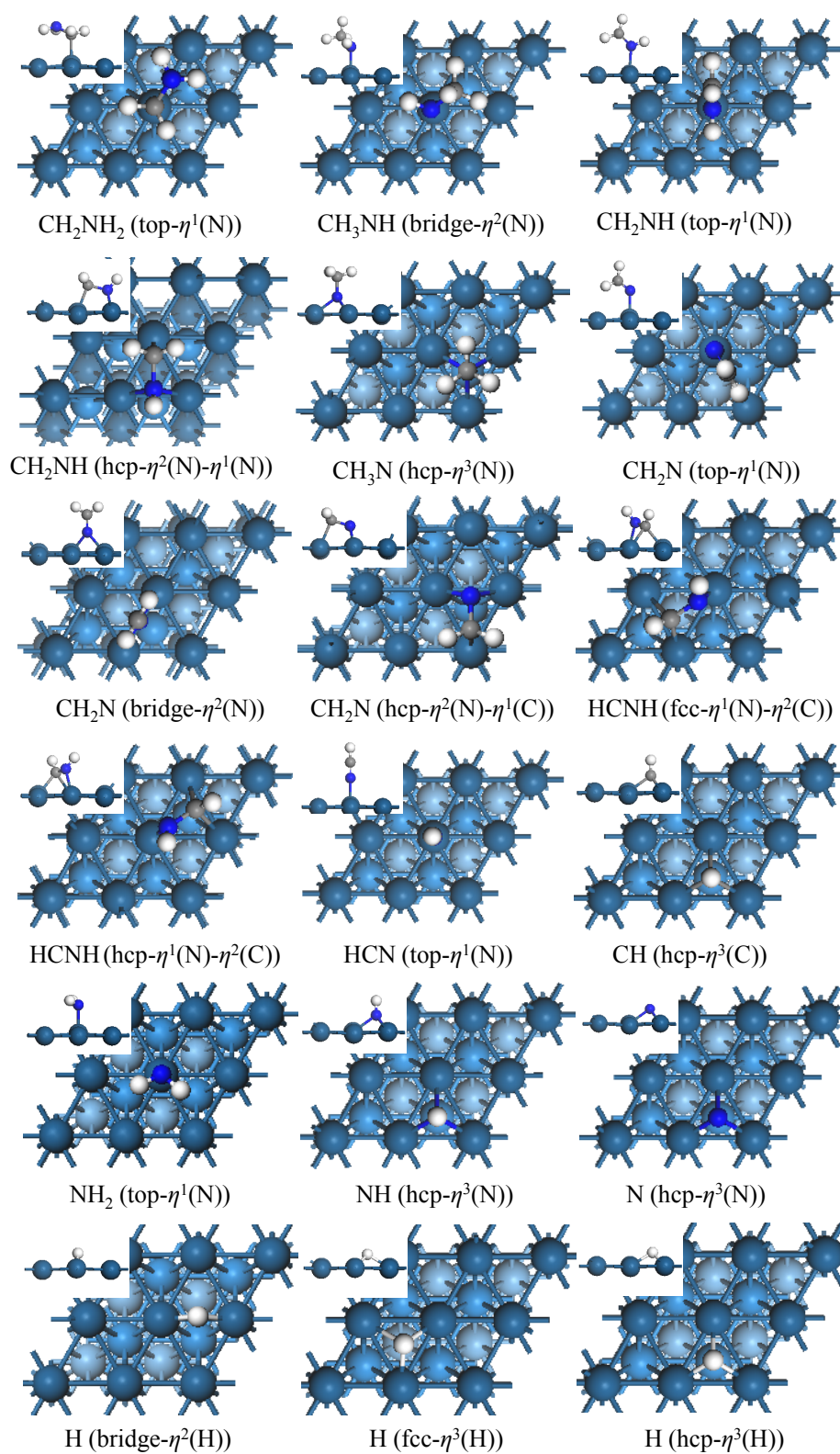


In order to understand the coverage effect, we have tested the adsorption of H, CH and NH with different coverage on Pt(111). The adsorption configurations and adsorption energies are shown in the following Fig. S1 and Table S1. As shown in Table, the adsorption energies of H, CH and NH at same site on (2×2) and (2×3) cell are almost equal, and the largest difference value, which come from CH adsorbed at hcp site on (2×2) and (2×3) cell, is only 0.06 eV (6.33 vs. 6.39 eV), which is far below the DFT itself deviation.

Table S1 Calculated adsorption energies for H, CH and NH on (2×2) and (2×3) Pt(111) surfaces.

Species	Configuration	E_{ads} on (2×2) cell	E_{ads} on (2×3) cell
H	top- η^1 (H)	2.85	2.86
	bridge- η^2 (H)	2.70	2.72
	fcc- η^3 (H)	2.70	2.73
	hcp- η^3 (H)	2.66	2.67
CH	fcc- η^3 (C)	6.46	6.51
	hcp- η^3 (C)	6.33	6.39
NH	fcc- η^3 (N)	3.89	3.90
	hcp- η^3 (N)	3.52	3.55

Fig. S2 The metastable adsorption configurations of intermediates involved in methylamine decompose to HCN on Pt(111).



CH₂NH₂ Decomposition. CH₂NH is one product of CH₂NH₂ decomposition via N–H bond scission.

CH₂NH₂ → CH₂NH + H. In the N–H bond activation, the reaction starts with CH₂NH₂ adsorbed at bridge site with $\eta^1(\text{N})-\eta^1(\text{C})$ mode, after the N–H bond scission, the CH₂NH fragment still stays the bridge site with $\eta^1(\text{N})-\eta^1(\text{C})$ mode and the H atom moves to a nearby top site in the FS. In the TS, CH₂NH is adsorbed at bridge site and the dissociated H atom is located at bridge site, the relevant N–H distance elongate to 1.533 Å from 1.022 Å in the IS. The reaction energy of this step is endothermic by 0.77 eV, and the energy barrier is 1.27 eV.

HCN Decomposition. HCN would be possible to further decompose to form CN and H, or CH and N through the C–H or C–N bond scission.

HCN → CN + H. In the process of HCN dehydrogenation, HCN locates at bridge site with the C–N bond paralleling to the surface. In the TS, the CN fragment still sits bridge site with $\eta^2(\text{C})$ configuration, the abstracted H locates hcp site with the C–H distance being 1.374 Å. In the FS, CN moves to top site with $\eta^1(\text{C})$ configuration, and the atomic H moves towards an adjacent top site. The energy barrier of this step is 1.50 eV, and the corresponding reaction energy is 0.32 eV.

$HCN \rightarrow CH + N$. The C–N bond scission starts with HCN at bridge site as the IS, ends with CH binding upright at hcp site via $\eta^3(C)$ configuration and the atomic N at fcc site as the FS. In the TS, CH moves to the neighboring bridge site and N remains at initial site, the relevant C–N distance increases to 1.852 Å. This step is endothermic by 1.51 eV and the barrier is 2.42 eV, indicating that the dehydrogenation of HCN is easier than that of the C–N bond scission.