Molecular dynamics (MD) simulations:

Molecular dynamics (MD) simulations at different temperatures were carried out to verify the interaction of H_2 with the Ni surface using the GULP of Material Studio 4.3 developed by Accelrys Software Inc.[1] In our MD simulation, 250 H_2 molecules and 512 Ni atoms were confined in a volume of 28.192 × 28.192 × 30 $Å^3$ as our initial model (see panel (a) of Fig. S-1). In the calculation, all of the Ni atoms were fixed and the H_2 molecules were allowed to move freely. The Compass potential function was used for the H_2 molecule.[2] Furthermore; the Morse potential form was applied to describe the interaction between the H atom and the Ni atom. The parameters of that potential were obtained by the Force-matching method (FMM),[3] and the reference data were calculated by the DFT. The parameters of the Morse potential function were listed in Table **S1**. The system was performed in Canonical ensemble (NVT). The Nose-Hoover thermostat was employed to maintain the system at different temperatures.[4] The total equilibration time of 60 ps was performed at five different temperatures (400, 500, 600, 800 and 1000 K). After reaching the equilibrated state, all systems were performed for 10 ps to collect the information for determining the number density distribution along the Z-axis.

To verify the interaction of H_2 with the Ni surface, MD simulations were performed at temperatures of 400 - 1000 K. The panel (b) of Fig. S-1 shows the number density distributions of H_2 molecules on Ni(100) (the substrate thick is about 6 Å) at five different temperatures. As temperature increasing, the peak of number density distributions was found to decrease by about 7 Å in the Z-direction. Furthermore, these peaks shifted slightly to the right side and intensity of number density distributions rose after the position of 7 Å in the Z-direction. This result reflects the fact the adsorption numbers of H_2 molecules on Ni substrate decreasing with

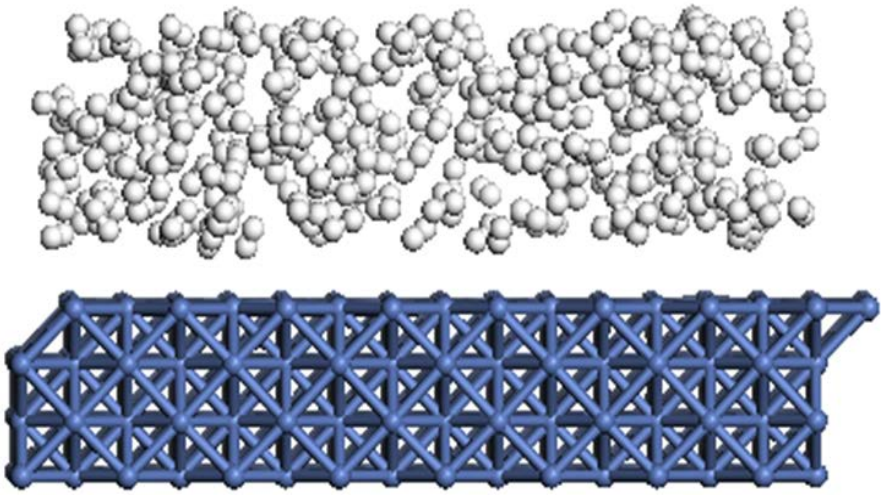
increasing temperature. In other words, our results indicate that a preferable temperature of H_2 molecules adsorbed on the Ni surface is at 400K in the temperature range of 400K–1000K.

References:

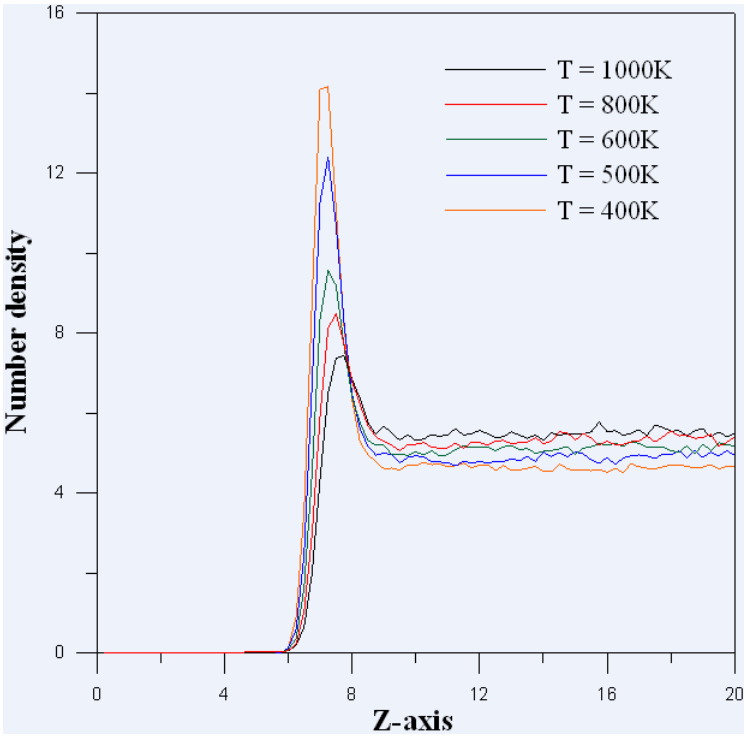
(1) MS Modeling 4.3; Accelrys Software Inc., http://www.accelrys.com.
(2) Yang, J. ; Ren, Y.; Tian, A. –m.; Sun, H.; *J. Phys. Chem. B*, **2000,***104*, 4951-4957.
(3) Ercolessi, F.; Adams, J. B.; *Europhys. Lett.* **1994**, *26*, 583-588.
(4) Allen, M. P.; Tildesley, D. J. Computer Simulation of Liquids, Oxford University Press, **1987**.

Table **S1**. The parameters of Morse potential function

	D(eV)	*a(Å^{-1})*	*r_0(Å)*
Morse	0.02	3.21	2.102



(a)



(b)

Figure S-1: (a) the initial model of H_2 on Ni(100) surface. (b) the number density distributions of H_2 molecules on Ni (100) at different temperatures.