

Downshift of Ni d band center at the Ni/Si₃N₄ hetero-interface

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Abstract

To investigate the influence of silicon nitride (Si₃N₄) catalytic support on the electronic metal-support interaction, we synthesized polymer-derived Ni nanoparticles embedded within an amorphous silicon nitride matrix (Ni/a-Si₃N₄) and an amorphous silicon dioxide matrix (Ni/a-SiO₂) samples through the polymer-derived ceramics route. Hydrogen (H₂) temperature-programmed-desorption profiles revealed that the Ni/a-Si₃N₄ sample had lower activation energy for H₂ desorption, compared with the Ni/a-SiO₂ system. Mechanistic study with the density functional theory calculation elucidated that the interfacial nickel-nitrogen interaction led to downshifting Ni d band center, which facilitates H₂ desorption experimentally observed in the Ni/a-Si₃N₄ sample.

1. Introduction

The adsorption strength between adsorbate (M_{ads}) and transition metal (TM) significantly influences catalytic performance.¹⁾ Electronic metal-support interaction (EMSI) at a hetero-interface plays a pivotal role in the adsorption strength of M_{ads}-TM since this interaction influences the electronic properties of TM.¹⁾ According to this principle, we have developed a research strategy that employs silicon nitride (Si₃N₄) as a catalytic support because its surface N atoms electronically interact with the loaded TM. To investigate the influence of Si₃N₄ catalytic support on the EMSI, we synthesized polymer-derived Ni nanoparticles loaded inside an amorphous silicon nitride matrix (Ni/a-Si₃N₄) on the one hand, and an amorphous silicon dioxide matrix (Ni/a-SiO₂). Hydrogen temperature-programmed-desorption (H₂-TPD) profiles for both samples revealed that the activation energy for H₂ desorption for the Ni/a-Si₃N₄ sample (47.4 kJ mol⁻¹) was lower than that for the Ni/a-SiO₂ sample (68.0 kJ mol⁻¹). To elucidate the influence of a-Si₃N₄ on the adsorption/desorption properties of Ni at a hetero-interface through the EMSI, the local electronic interaction around the Ni/matrix hetero-interface was evaluated with a set of models theoretically predicted by the density functional theory (DFT) calculations.

2. Experiment

All spin-polarized DFT calculations were performed with the Quantum ESPRESSO package. In all calculations, kinetic energy cutoffs used to represent the electron wave function and charge density are 544 eV (40 Ry) and 6802 eV (500 Ry), respectively. The Fermi surface was broadened using a gaussian smearing parameter of 0.204 eV. The Brillouin zone was sampled by the Monkhorst-Pack k-point grid, with the reciprocal lattice spacing $\approx 0.2 \text{ \AA}^{-1}$ for structural relaxation. For optimized structures, we analyzed the projected density of states (pDOS) by non-self-consistent field calculations with the reciprocal lattice spacing $\approx 0.1 \text{ \AA}^{-1}$. For the investigation of interfacial phenomena, the supercells for Ni/ β -Si₃N₄ and Ni/ α -SiO₂ were constructed using the Ni (111) slab model since this plane is the most stable one in fcc Ni. For the Ni (111)/ β -Si₃N₄ interface model, the Ni (111) slab model with 7 layers was laid on the β -

Si₃N₄ (001) slab model with 9 layers. Similarly, for the Ni (111)/ α -SiO₂ interface model, the Ni (111) slab model with 7 layers was laid on the O-terminated α -SiO₂ (001) slab model with a thickness of 4 units. The projected crystal orbital Hamilton populations (pCOHP) were calculated to investigate the bonding nature at a hetero-interface by using the Local-Orbital Basis Suite Toward Electronic-Structure Reconstruction package (LOBSTER).

3. Results and discussion

The pDOS onto the interfacial Ni 3d orbitals of two distinct Ni/ β -Si₃N₄ and Ni/ α -SiO₂ interfacial models was depicted in Fig. 1. The pDOS revealed that the values of d band center for both spin-up (ϵ_d^\uparrow) and spin-down (ϵ_d^\downarrow) relative to the Fermi energy in the Ni/ β -Si₃N₄ model are distant from the Fermi level, compared with those in the Ni/ α -SiO₂ model. According to the d band theory,²⁾ the downshift of the d band center relative to the Fermi energy means that the less availability of empty antibonding states between the M_{ads} and TM results in weaker interactions. Thus, this downshift of the interfacial Ni d band center facilitated the hydrogen desorption experimentally observed in the Ni/a-Si₃N₄ sample. The pCOHP analysis was performed to investigate the bonding natures of Ni-N and Ni-O in the Ni/ β -Si₃N₄ and Ni/ α -SiO₂ interfacial models, respectively. The average integrated -COHP (-ICOHP) up to the Fermi level over the Ni-N and Ni-O bonds is listed in Table 1. In general, the greater the positive -ICOHP for a bond is, the more covalent nature of the bond is.³⁾ Thus, Table 1 confirms that more covalent bonds are generated, regardless of spin-up and spin-down states, between interfacial Ni and N, which is potentially driven by the lower electronegativity of the N atom compared to that of the O atom. It should be noted that such a strong orbital hybridization can broaden the d band and downshift the d band center of metal.⁴⁾ Therefore, we can predict from the DFT calculations that the Ni at heterointerface in the Ni/ β -Si₃N₄ interface has a weaker interaction towards an adsorbate which leads to the facilitated H₂ desorption property observed for the polymer-derived Ni/a-Si₃N₄ in this study.

4. Conclusions

In this work, the EMSI between Ni nanoparticles and a-Si₃N₄ matrix was deeply investigated by experimental and theoretical studies. H₂-TPD profiles indicated the activation energy for H₂ desorption for the Ni/a-Si₃N₄ sample was lower than that for the Ni/a-SiO₂ sample. DFT calculations using the two distinct Ni/ β -Si₃N₄ and Ni/ α -SiO₂ interfacial models elucidated that the strong hybridization between the Ni and N at hetero-interface exhibited the more covalent natures. The strong hybridization of Ni and N resulted in the further downshift of the Ni d band center at Ni nanoparticles/a-Si₃N₄ hetero-interfaces. Thus, this downshift of Ni d band center resulted in facilitated hydrogen desorption experimentally observed for the Ni/a-Si₃N₄ sample.

References

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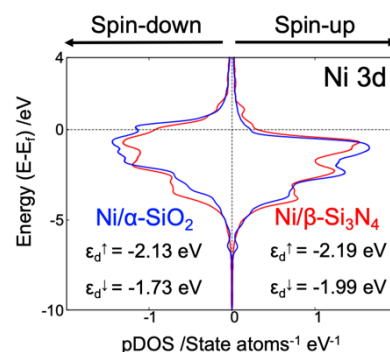


Fig. 1. pDOS of Ni 3d orbitals of the hetero-interfacial region for the Ni/ β -Si₃N₄ (red-line) and Ni/a-SiO₂ (blue-line) models.

Table 1. -ICOHP values for spin-up and spin-down states of Ni-N and Ni-O bonds at hetero-interface for the Ni/ β -Si₃N₄ and Ni/a-SiO₂ models.

	Spin-up	Spin-down
Ni-N	0.69	0.83
Ni-O	0.51	0.71