Surface studies of H_2S adsorption on bimetallic NiM (111) surfaces

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Introduction

Steam reforming of the tars produced during biomass gasification requires the use of a catalyst. Supported nickel has been proven to be an excellent catalyst for this application [1]. However, a major issue in the long term stability and activity of the catalyst is its tolerance towards small (ppm) levels of sulfur-containing compounds, including H_2S, present in the process feed stream [2]. Sulfur is known to bind very strongly on the active Ni surface, blocking sites required for the reforming reaction [3]. In some systems, sulfur has also been associated with significant metal restructuring and bulk sulfide formation, which lowers the long term catalyst stability and regenerability [4].

Several studies have indicated that Ni containing bimetallic alloys change the energetics of reactions considerably. Nikolla *et al.* have recently studied the contribution of alloying in improving the long term stability of Ni reforming catalysts [5]. They found that the carbon tolerance of some Ni-containing alloys (such as NiSn) is far better than that of monometallic Ni.

Our work revolves around improving the sulfur tolerance of Ni catalysts. In the current work, we use density functional theory (DFT) calculations to understand H_2S adsorption and dissociation on strained Ni (111) surfaces with a non-equilibrium lattice constant x (Ni_x), Ni_3M/Ni (111) surface alloys and Ni_3M (111) homogenous alloys (M = Sn, Pd, Pt, Ru). The objective has been to understand the contribution of strain and ligand effects in the alteration of H_2S decomposition on Ni alloy surfaces. Results have been used to suggest designs for supported catalysts, which have been prepared and screened in a bench-scale reactor.

Materials and Methods

H_2S adsorption and decomposition on various surfaces was studied using density functional theory calculations performed using the Vienna Ab-initio Simulation Package [6, 7]. The Kohn-Sham one electron valence states were expanded in a plane wave basis set using the projector augmented wave (PAW) method [8]. A cutoff energy of 350 eV was used in the expansion of the basis set. The surface calculations were performed on slabs with a thickness of four atomic layers. We used 2x2 unit cells for the surface calculations and the adsorbate coverage examined is 0.25 ML. Catalysts were prepared using the incipient wetness impregnation technique on an alumina (Al_2O_3) support. The catalysts were then tested for their H_2S tolerance in a bench-scale steam reforming reaction system.

Results and Discussion

Our results indicate that the Ni_3Sn/Ni(111) surface alloy is most sulfur tolerant and Ni_3Pd and Ni_3Pt are the least sulfur tolerant alloys of all the combinations studied to date. We investigated the effect of varying lattice constant on sulfur tolerance and concluded that the adsorption energy of sulfur is approximately linearly dependent on the lattice spacing (Fig 1). Our results indicate that the d-band center, which is the weighted average of the d-band, varies linearly with lattice constant. This implies that the strain affects the electronic structure of the surface. Ligand influenced d-band changes, which affect the DOS at Fermi level, also explain the trends we found in H_2S adsorption and decomposition. In the case of Ni_3Pd and Ni_3Pt, unlike in Ni_3Sn/Ni(111), most of the electrons are concentrated near the Fermi level. Thus, Ni_3Pd and Ni_3Pt surfaces have more electrons available for binding as compared to Ni_3Sn/Ni(111). The preliminary reaction results for the Ni/Al_2O_3, Ni-Ru/Al_2O_3, and Ni-Mg/Al_2O_3 catalysts during syngas reforming shows an enhanced sulfur tolerance for Ni-Ru/Al_2O_3 and Ni-Mg/Al_2O_3. Preliminary results seeking to address the especially high sulfur tolerance of Mg-promoted catalysts will be presented.

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Significance

Biofuels produced from biomass gasification hold great promise as a domestic renewable and sustainable energy resource [9]. Tar cracking and reforming, which involves the use of a catalyst, increases the efficiency of biomass thermochemical conversion [10].

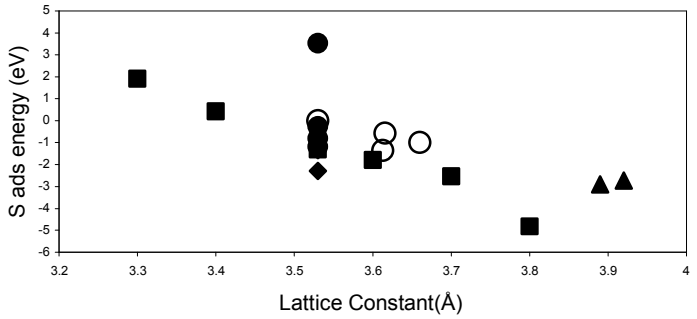

Figure 1: S adsorption energy as a function of lattice constant. Squares indicate Ni_x surfaces, the filled circles indicate M/Ni (111) surfaces, and open circles indicate Ni_3M, rhombus indicates M/Ni (111) overlayers and triangles indicate Ni/M(111).

References

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