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A density functional theory study of HCN hydrogenation to methylamine on Co(111)

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Abstract

The hydrogenation of HCN to methylamine on Co(111) was used as a model reaction to study the hydrogenation of nitriles to primary amines. Density functional theory was used to characterize the reaction mechanism, and the results obtained were compared with those for the same reaction on Ni(111). Hydrogen cyanide adsorbs more strongly on Co(111) than on Ni(111), with an adsorption energy of −1.72 eV. The hydrogenation product, methylamine, is weakly adsorbed on Co(111), with an adsorption energy of −0.53 eV, which is very similar to the adsorption energy calculated on Ni(111). The calculated adsorption energies were used to explain the differences in activity and selectivity observed between nickel- and cobalt-based catalysts; the stronger adsorption of HCN on cobalt explains both the lower activity and the higher selectivity observed on this metal. Regarding the reaction mechanism, the hydrogenation reaction implies an imine intermediate (H_2CNH) independent of whether hydrogen reacts with the carbon atom or with the nitrogen atom of the hydrogen cyanide molecule in the first step. The imine intermediate subsequently reacts to form H_3CNH, which is finally hydrogenated to yield methylamine. The overall surface reaction is endothermic. Remarkably, comparing the HCN hydrogenation reaction mechanism on Co(111) and Ni(111) revealed no significant differences.

Keywords: Hydrogenation; Nitriles; Cobalt; Nickel; DFT; Hydrogen cyanide; Methylamine

1. Introduction

The hydrogenation of different nitriles in the liquid phase and at elevated hydrogen pressures is used in the chemicals industry to prepare different important amines. When primary amines are the desired product, the use of nickel and cobalt catalysts is recommended [1]. Although the activity and selectivity of these catalysts are known to differ, the reason for these differences is not yet properly understood [2]. Regarding the reaction mechanism of this process, it is well known that the hydrogenation of nitriles to give primary amines evolves through an imine intermediate, which can condensate with the final primary amine to give secondary amines as byproducts [3]. The formation of secondary amines also involves a secondary imine as an intermediate.

The literature reports a higher content of secondary amines n the literature when a Ni-based catalyst is used instead of a Co-based one; this is valid for both pure metal catalysts and Raney catalysts [1]. In the hydrogenation of palmitonitrile, adiponitrile, and butyronitrile, it was concluded that the higher content in secondary amines observed when using a nickel catalyst instead of a cobalt catalyst was due to the stronger adsorption of the products on nickel. On the other hand, experiments conducted on different nickel and cobalt catalysts for the hydrogenation of lauronitrile showed that the secondary amine was formed by hydrogenation of the secondary imine during the whole experiment on nickel, but at just the end of the reaction on cobalt. The accumulation of the imine intermediate on cobalt in those experiments was explained by a stronger adsorption of the nitrile on this metal [1]. The different adsorption strengths of the nitrile and primary amine were also used to

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justify the higher selectivity of cobalt catalysts in a study of acetonitrile hydrogenation with nickel and cobalt catalysts alloyed with boron [4]. Other factors have also been considered to justify the differences in selectivity between nickel and cobalt catalyst [1], those studies concluded that selectivity does not depend on the method of catalyst preparation, support used, or catalyst concentration; although there is still some discussion about the effect of the support [2,5].

Although the selectivity toward primary amine formation is higher on Co than on Ni, activity is lower on the former. The initial reaction rate (as the rate of hydrogen consumption) per unit surface area of the metal is 20:10:1 for Ni, Co, and Cu [1]. This observation has also been explained in terms of stronger adsorption of the nitrile reactant on cobalt, which may inhibit the competitive hydrogen adsorption, giving a lower activity on this metal [4].

To summarize, the differences in activity and selectivity observed experimentally in the hydrogenation of nitriles to primary amines between nickel and cobalt-based catalysts have been explained by the following arguments: (1) the stronger adsorption of the nitrile on cobalt accounts for the lower activity on cobalt-based catalysts; (2) the stronger adsorption of the nitrile on cobalt also accounts for the larger selectivity toward primary amines of cobalt catalysts by impeding condensation reactions between the intermediate imine and primary amines to secondary amines; and (3) the selectivity toward primary amines is greater on cobalt catalysts because the primary amine is less strongly adsorbed on cobalt.

The present study used density functional theory (DFT) to study the hydrogenation of nitriles to primary amines on cobalt catalysts and compared the results thus obtained with those reported in a similar study on nickel [6]. The final aim of these calculations was to verify the hypothesis argued in the literature to justify some of the differences observed between nickel- and cobalt-based catalysts.

2. Computational details

We used the Vienna *ab initio* simulation package (VASP) [7,8], which performs an iterative solution of the Kohn–Sham equations in a plane wave basis set. Plane waves with kinetic energy $\leqslant 300$ eV were included in the calculation. The exchange-correlation energy was calculated within the generalized gradient approximation (GGA) using the form of the functional proposed by Perdew and Wang [9,10], usually referred to as Perdew–Wang 91 (PW91). The electron–ion interactions for C, N, H, and Co were described by the projector-augmented wave (PAW) method developed by Blöchl [11]. This is essentially an all-electron frozen core method combining the accuracy of all-electron methods and the computational simplicity of the pseudopotential approach, particularly in the implementation of Kresse and Joubert [12]. A first-order Methfessel–Paxton smearing function with a width of about 0.1 eV was used to account for fractional occupancies [13]. Spin-polarized calculations were done to account for the magnetic properties of cobalt. Initially, the relative positions of the metal atoms were fixed as those in the bulk, with an optimized lattice parameter of 3.5207 Å for FCC cobalt. The optimized lattice parameter was calculated using the smallest unit cell possible for modeling the bulk of FCC Co, and its reciprocal space was sampled with a $(15 \times 15 \times 15)$ k-point grid generated automatically using the Monkhorst–Pack method [14].

The Co(111) surface was modeled with a four-layer slab model with four cobalt atoms per layer representing a $p(2 \times 2)$ surface unit cell and a vacuum region of $\sim$10 Å. The reciprocal space of the $p(2 \times 2)$ unit cell was sampled with a $(5 \times 5 \times 1)$ k-points grid generated automatically using the Monkhorst–Pack method. Partial geometry optimizations were performed, including relaxation of the first metal layer, using the RMM–DIIS algorithm [15]. In this method, the forces on the atoms and the stress tensor were used to determine the search directions for finding the equilibrium positions. Geometry optimizations were stopped when the difference in the total energy in two consecutive steps was <0.001 eV. The transition states were located in two steps: (1) using the climbing-image nudget elastic band method (CI-NEB) [16] to find likely transition state structures, and (2) refining the structure of the transition state by performing a geometry optimization calculation using a convergence criterion based on the forces acting on the atoms. The transition state structure was deemed converged when the forces acting on the atoms were all <0.04 eV/Å for the various degrees of freedom set in the calculation. The molecules in the gas phase (needed to obtain adsorption energies) were calculated using a $10 \times 10 \times 10$ Å^3 cubic unit cell. Spin-polarized calculations were done when needed.

3. Results and discussion

3.1. Hydrogen cyanide (HC≡N)

Several configurations were considered for HCN adsorbed on Co(111). HCN is likely to adsorb either perpendicularly to the surface through the lone-pair of the nitrogen atom or flat with the CN bond parallel or tilted with respect to the metal surface. Different adsorption sites were studied for these orientations: top (t), bridge (b), and hollow hcp (h) and fcc (f).

As was found for HCN adsorbed on Ni(111) [6], the parallel adsorption modes were energetically favored over the perpendicular ones (Table 1). The most stable adsorption state for HCN involved two adjacent hcp and fcc 3-fold hollow sites; hereinafter, this is designated h-η^3(N)-f-η^3(C); $\eta^k(X)$ indicates that atom X interacts with k-surface atoms. As on Ni(111), both h-η^3(N)-f-η^3(C) and f-η^3(N)-h-η^3(C) configurations showed similar adsorption energies. The adsorption energy of the most stable state [h-η^3(N)-f-η^3(C)] on Co(111) was -1.72 eV, which is 0.22 eV more stable than the most stable adsorption mode found on Ni(111). Therefore, HCN is more strongly adsorbed on Co(111) than on Ni(111), which confirms a previous experimental hypothesis about the stronger adsorption of the nitrile group on cobalt catalysts [1,4].

As was found for Ni(111), a quite elongated CN bond was obtained for HCN adsorbed on a h-η^3(N)-f-η^3(C) site. The CN distance was 1.34 Å for HCN adsorbed on this site, whereas on the gas phase geometry [17], it was 1.16 Å (elongation of