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Ethylene dissociation on flat and stepped Ni(1 1 1): A combined STM and DFT study

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Abstract

The dissociative adsorption of ethylene (C_2H_4) on Ni(1 1 1) was studied by scanning tunneling microscopy (STM) and density functional theory (DFT) calculations. The STM studies reveal that ethylene decomposes exclusively at the step edges at room temperature. However, the step edge sites are poisoned by the reaction products and thus only a small brim of decomposed ethylene is formed. At 500 K decomposition on the (1 1 1) facets leads to a continuous growth of carbidic islands, which nucleate along the step edges.

DFT calculations were performed for several intermediate steps in the decomposition of ethylene on both Ni(1 1 1) and the stepped Ni(2 1 1) surface. In general the Ni(2 1 1) surface is found to have a higher reactivity than the Ni(1 1 1) surface. Furthermore, the calculations show that the influence of step edge atoms is very different for the different reaction pathways. In particular the barrier for dissociation is lowered significantly more than the barrier for dehydrogenation, and this is of great importance for the bond-breaking selectivity of Ni surfaces.

The influence of step edges was also probed by evaporating Ag onto the Ni(1 1 1) surface. STM shows that the room temperature evaporation leads to a step flow growth of Ag islands, and a subsequent annealing at 800 K causes the Ag atoms to completely wet the step edges of Ni(1 1 1). The blocking of the step edges is shown to prevent all decomposition

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of ethylene at room temperature, whereas the terrace site decomposition at 500 K is confirmed to be unaffected by the Ag atoms.

Finally a high surface area NiAg alloy catalyst supported on $MgAl_2O_4$ was synthesized and tested in flow reactor measurements. The NiAg catalyst has a much lower activity for ethane hydrogenolysis than a similar Ni catalyst, which can be rationalized by the STM and DFT results.

Keywords: Nickel; Single crystal surfaces; Steps; Alkenes; Catalysis; Scanning tunneling microscopy; Density functional calculations; Surface chemical reaction

1. Introduction

Ever since the work by Taylor in 1925, the concept of active sites for reactions at metal surfaces has been an important notion within the field of heterogeneous catalysis [1]. Gwathmey et al. made extensive studies on the influence of the crystal face on catalytic reactions [2], and Yates et al. [3] used stepped single crystal surfaces to study the role of step edges in surface chemical reactions. Following the advent of scanning probe microscopy Zambelli et al. [4] were able to provide direct evidence that the step edges are the active sites for the NO dissociation on Ru(0001). Dahl et al. [5] quantified the effect for N_2 dissociation on Ru(0001) by using density functional theory calculations (DFT) and detailed experiments to show that dissociation at the step edges has an activation energy which is more than 1 eV lower than that on the terraces at 500 K. Since then DFT calculations and experiments have shown that step edges in general are more reactive towards the dissociation of a number of simple diatomic molecules such as CO, NO, O_2, and N_2 [6–10]. For more complicated molecules the reactivity is not the only important factor, and in particular the selectivity of a surface for a given reaction must also be taken into account.

Recently, we demonstrated that the bond-breaking selectivity for the ethylene (C_2H_4) decomposition on Ni(111) is to a high degree influenced by the presence of free step edges [11]. In the present paper, we provide further insight into this reaction based on STM experiments, DFT calculations and flow reactor measurements. We show that the step edges of a Ni(111) surface are indeed more reactive than the (111) facets. The step edge sites are active for ethylene decomposition at room temperature, whereas the regular terrace atoms become active only at higher temperatures. In addition we take two further steps. First, we show that the higher reactivity of the step edges is much more pronounced for C–C bond breaking than for C–H bond breaking. This means that the number of step sites plays an important role in the selectivity of hydrogenation, dehydrogenation, and hydrogenolysis (C–C bond breaking) reactions. Second, we show that the steps can be blocked selectively by the deposition of small amounts of Ag on the Ni(111) surface. The conclusion is that the number of reactive step sites can be controlled, which may be used in the design of catalysts with a specific selectivity. This approach is exploited in the synthesis of a high surface area AgNi alloy catalyst, which is compared to both a pure Ni and a CuNi catalyst in hydrogenolysis experiments.

2. Methods

2.1. Experiment

The STM experiments were conducted in an ultrahigh vacuum (UHV) chamber equipped with standard sample preparation and surface science analysis tools, and a home-built Aarhus STM [12,13]. The sample was exposed to ethylene (Praxair 99.95%) by backfilling the chamber with the sample kept at a constant temperature. Subsequently the sample was allowed to cool to room temperature before being transferred to the STM.

The crystal was cleaned on a daily basis by sputtering (2 keV Ar^+) and annealing (800 K) cycles, and whenever needed oxidation/reduction cycles