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Dynamic nucleation and growth of Ni nanoparticles on high-surface area titania

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Abstract

Nucleation and growth mechanisms of Ni nanoparticles synthesized via an incipient wetness technique on a high-surface area titania support (i.e., a mixture of anatase and rutile) are studied using environmental transmission electron microscope (ETEM). Most Ni nanoparticles are found to nucleate from the Ni precursor coated on the surface of the titania support. Even though both anatase and rutile supports are the nucleation sites for Ni nanoparticles, it was observed that the particles have different morphologies on the supports, i.e., a non-wetting morphology on the anatase support versus a wetting morphology on the rutile {1 0 1}. This is because the interfacial energy of Ni/rutile is lower than that of Ni/anatase. Titania clusters are found to nucleate on the surface of the Ni particles during in situ ETEM reduction, indicating that the presence of partial titania overlayers is directly related to the synthesis of the Ni/TiO_2 catalysts. The growth mode of the Ni nanoparticles on the titania support is three-dimensional, while that of the rutile cluster on the surface of the Ni is two-dimensional layer-by-layer.

Keywords: Ni; Titanium oxide; Anatase; Rutile; Nucleation; Growth; Morphology; Reduction; Synthesis; Environmental TEM; Nanoparticles; Catalysts

1. Introduction

A considerable body of work [1–6] has been carried out on the nucleation and growth of metal clusters on single crystal oxide surfaces due to the extensive applications of metal/oxide systems to heterogeneous catalysts. However, in many practical applications, heterogeneous catalysts are synthesized via an incipient wetness technique on a high-surface area oxide support [7]. This approach uses a combination of wet chemistry and reducing atmospheres to create a dispersion of metal particles and is very different from the ultra-high vacuum (UHV) evaporation techniques used in most of the single crystal work. Very few atomic level studies have been undertaken to understand the fundamental physical processes taking place during such synthesis. This is partly due to the complex nature of the high-surface area supports, which may consist of particles with different sizes, crystal facets and structures. The problem is compounded by the lack of suitable in situ techniques for studying the transformation process under suitably high gas pressures.

Ni is an important transition metal that is used in many heterogeneous catalysts. In many applications, Ni is loaded on a reducible oxide support like titania. There are a significant number of surface science studies conducted under UHV conditions on the {1 1 0} rutile surface [1–6,8,9]. However, in catalytic applications, the metal is usually loaded onto a suitable high-surface area titania. One of the more commonly used titanias is Degussa P25 consisting of 75% anatase and 25% rutile grains [10]. It was suggested that Ni nanoparticles grow three-dimensionally on rutile

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supports [2]. However, the growth mechanism of Ni nanoparticles on anatase grains does not appear to have been studied. There are many questions surrounding the nucleation and growth of Ni nanoparticles on the surface of these industrially important high-surface area titanias. Does the precursor uniformly spread over the surface of the support? Is the precursor mobile when heated in a reducing environment? Where are the nucleation sites for metal particle growth? Does the precursor transform directly to metal or are intermediate compounds first formed? These question and many others remain about not just the Ni on titania but also many other catalytic metal/support combinations.

Environmental transmission electron microscopy (ETEM) is a suitable technique for studying the nucleation and growth of metal nanoparticles on a high-surface area support. The technique allows us to study gas–solid reactions at atomic level with pressures up to a few Torr [10–15] and temperatures up to 800 °C. It is ideal for studying reactions on high-surface area supports because the evolution of individual metal nanoparticles on particular grains of titania can be followed during in situ reduction of the precursor. We have already demonstrated that ETEM can be applied to investigate the in situ synthesis of Ni nanoparticles from heavy Ni precursor loadings (i.e., 10 wt.%) supported on high-surface area titania [10]. In that study, Ni precursor, loaded by the incipient wetness technique, was found to distribute non-uniformly on the titania support and large patches of Ni precursor acted as nucleation centers for the Ni nanoparticle growth [10]. Most Ni particles were found to possess a non-wetting morphology on the titania support [10]. Modification of the particle equilibrium shape under different gas conditions was also explored [10].

Here we are interested in studying the nucleation and growth process under lower, more realistic metal loadings (3 wt.%). In the present study, we report on the mechanism, at the atomic scale, of the dynamic nucleation and growth of Ni nanoparticles on both anatase and rutile grains. The wetting/non-wetting behavior of the Ni nanoparticles on rutile/anatase supports is discussed in detail. The growth mode of the Ni nanoparticles on rutile and anatase supports is discussed in terms of the surface and interface energies. The growth mode of the Ni nanoparticles on a high-surface area rutile support is compared with UHV single crystal studies. We also observe a double nucleation event in which rutile simultaneously nucleates on the surface of the growing Ni particle. This observation provides evidence for the decoration model proposed [16] to explain the strong metal support interaction (SMSI) associated with metal nanoparticles on reducible oxide supports. The relevance of this decoration model for SMSI phenomena is discussed.

2. Experimental procedures

2.1. Preparation of precursor

Degussa P-25 (titanium dioxide with a mixture of about 75% anatase and 25% rutile) was loaded with 3 wt.% Ni by an incipient wetness technique. An aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$ was added to fill the pores of a certain amount of titania support during constant mixing. After the solution was added, the wet mass was left on an evaporating dish for 30 min in open air. The material was then dried in air at 120 °C for 16 h in a drying oven. Precursor specimens for ETEM were prepared by placing the powders on 50-mesh Pt grids with 99.997% purity.

2.2. In situ synthesis of Ni metal nanoparticles

To study the dynamic nucleation and growth mechanism of the Ni nanoparticles, the $Ni(NO_3)_2 \cdot 6(H_2O)$ was reduced in situ using a Tecnai F-20 field emission ETEM operating at 200 kV. The microscope has a Scherzer resolution of 0.24 nm with an information limit of 0.12 nm. Precursor samples were loaded into an Inconel heating holder and inserted into the built-in environmental cell between the objective lens pole pieces of the microscope. This arrangement allows us to study the chemical reactions between gas molecules and nanoparticles at reasonably high pressures and reaction temperatures without compromising the atomic resolution imaging capability of the transmission electron microscope (TEM).

In situ metal particle synthesis was carried out by reducing the $Ni(NO_3)_2 \cdot 6(H_2O)$ in 0.2 Torr of CO in the ETEM. The precursor was rapidly heated to 350 °C over a period of 5 min and kept at this temperature in the CO atmosphere for 5 h. For this precursor, CO is a stronger reducing agent than H_2 and leads to an easier reduction of precursor at lower pressures. Comparison of experiments conducted in H_2 and CO show no evidence for the precursor reduction being strongly influenced by the formation of $Ni(CO)_4$. In addition, the boiling point of $Ni(CO)_4$ is 43 °C and we anticipated that it rapidly decomposes at the reduction temperature employed here (i.e., 350 °C).

The dynamic reduction process of the precursor (i.e., nucleation and growth of Ni nanoparticles) was recorded using a high-resolution camera. Since the formation of individual Ni particles was followed at the atomic level to understand the dynamic reduction process, we were normally able to analyze about 20–30 nucleation and growth events by conducting the experiments under the same reducing condition twice. In order to avoid the strong electron beam introduced artifacts to our experiments, very low electron doses were used to observe the precursor reduction process with some sacrifices of the quality of the high-resolution electron microscopy (HREM) images. HREM images from different areas of the sample were extracted frame by frame from the digital videotape using the IMovie™ software. In some cases, a four-frame averaging process was used to reduce noise. HREM images were also acquired from a CCD camera using DigitalMicrograph 3.1™ software during the ETEM experiments.

The shape of the Ni particles can be clearly determined if the Ni particles locate on the titania surfaces with edge-on orientation, i.e., the titania surface paralleled to the elec-