

Structural Changes in Nanoparticle Catalysts as Monitored by Their Magnetic Properties**

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Scanning probe microscopies, transmission electron microscopy, and other spectroscopic techniques have been successfully applied to accumulate structural information on nanoparticle catalysts.^[1-5] Even though these methods provide data at the atomic level, it has not been possible so far to unravel all details necessary to establish structure–reactivity relationships. One problem is the presence of several interfaces in such systems, that is, the particle–gas and the particle–support interfaces. As a result, the search for analytical tools with sufficient sensitivity is ongoing. It has long been recognized that small changes in the structure influence the magnetic properties drastically (see, for example, reference [6,7]). Therefore, monitoring magnetic properties of these systems could help to provide deeper insight into structure–reactivity relationships. Some processes in nanoparticle catalysts that can be probed by the magnetic properties of the system are illustrated schematically in Figure 1.

The adsorption of molecules is the primary step of a surface reaction. Although ferromagnetism is a bulk property, it will be shown that the magnetic properties are extremely sensitive to the adsorption process (Figure 1, route A). In addition, the method provides access to properties of the particle–substrate interface (route B). It can be used, for

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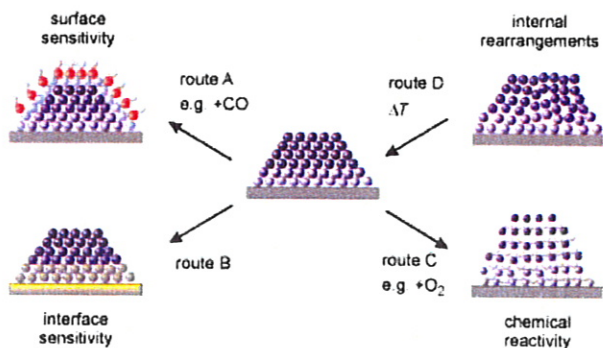


Figure 1. Schematic representation of different processes monitored by magnetic properties.

example, to monitor chemical reactions between the supported metal particle and the substrate. More generally, chemical modifications of the particles caused by reactions with a gas atmosphere can be identified by changes in the magnetic properties (route C). In dispersed catalytic systems, thermal stability of the nanoparticles is an important factor. Besides a sintering of particles—that is, a redistribution of atoms between particles at elevated temperatures—internal rearrangements such as a crystallization of the particles may be important (route D). It has been shown for model catalysts that structural characteristics determine important properties such as the adsorption sites of molecules from the gas phase.^[8] Both effects, namely, interparticle as well as intraparticle redistributions, can be studied. Given that magnetic properties can be recorded in situ, the sensitivity to these processes provides unique opportunities in catalytic research.

Electron spin resonance (EPR) spectroscopy (usually called ferromagnetic resonance (FMR) in the case of ferromagnetic systems) has proved to be a valuable tool for both powder catalysts and single crystal surfaces.^[9–12] It was used under ultrahigh-vacuum (UHV) conditions to characterize the ferromagnetic properties of Ni and Co nanoparticles on well-defined Al_2O_3 surfaces. In the following we want to focus the discussion on the interfacial sensitivity of this method. The sensitivity to adsorption of molecules at the metal–vacuum interface as well as the sensitivity towards the metal–substrate interface will be shown by two examples. In particular, the latter interface is difficult to access with other methods.

Nickel particles with a lateral size of 60–250 nm and an average height of 9 nm, based on scanning electron microscopy (SEM; Figure 2), were prepared by depositing the equivalent of a 14-Å thick Ni layer onto an $\alpha\text{-Al}_2\text{O}_3$ (11 $\bar{2}$ 0) surface at room temperature and subsequent annealing to 900 K. The low-energy electron diffraction pattern shows hexagonal spots of Ni crystallites in the (111) orientation as well as rectangular spots of the underlying (11 $\bar{2}$ 0) surface. The (111) facets exhibit the lattice spacing of bulk Ni, indicating a

relaxation of the uniaxial lattice mismatch of 11% along the (1 $\bar{1}$ 00) direction of the $\alpha\text{-Al}_2\text{O}_3$ crystal in the top layers of the Ni particles (the lattice constant in the (0001) direction of the $\alpha\text{-Al}_2\text{O}_3$ surface fits almost perfectly to Ni(111)).^[13]

The prepared surface was exposed to CO. The diagram on the left-hand side of Figure 2 shows the positions of the three signals in the FMR spectra as a function of CO dosage. The measurements were made with the static magnetic field perpendicular to the surface. Owing to the overlap of the three signals the resonance positions were determined by assuming a symmetric line shape. The weak signal at 5500 G was assigned on the basis of temperature-dependent measurements, which clearly reveal a doublet of lines. Above 0.4 L of CO (1 L = 10^{-6} torrs) this line

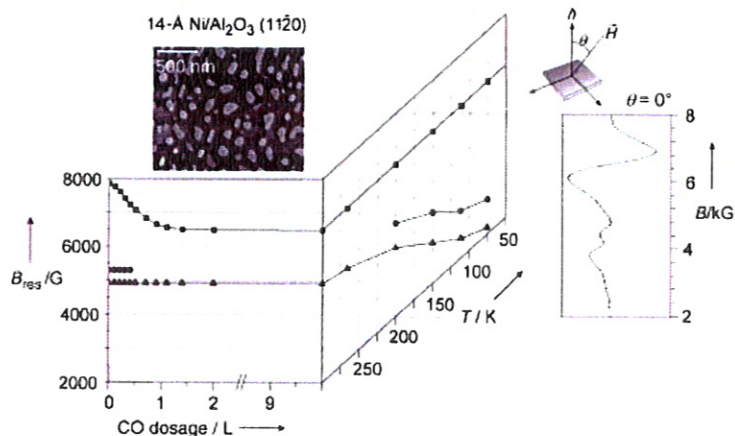


Figure 2. Left: Resonance positions measured for 14-Å Ni on an $\alpha\text{-Al}_2\text{O}_3$ (11 $\bar{2}$ 0) surface as a function of CO dosage. Right: Resonance positions for the CO-saturated state as a function of the substrate temperature. The measurements were made at normal incidence of the static magnetic field. The spectrum shown was measured at 200 K. Inset: an SEM image of the sample ($1.8 \times 1.5 \mu\text{m}^2$).

overlaps with the intense high-field absorption; this prevents a reliable determination of the resonance position. Although the proportion of surface atoms in particles of this size is relatively low, the high-field resonance exhibits a strong dependence of the resonance position on CO adsorption. In contrast to the high-field resonance the two resonances at lower field are unaffected within the resolution of the experiment. The shift of the high-field line renders the sensitivity range from approximately 0.05 L up to saturation coverage at 1 L. After desorption of CO at elevated temperatures the resonance position of the pristine particles is restored, which proves this process to be reversible. It should be noted that adsorption of hydrogen has the same effect as CO adsorption.

The situation is exactly reversed if the temperature dependence is considered. With decreasing temperature the two low-field resonances shift strongly towards lower fields, whereas the resonance at high field is basically unaffected (Figure 2, right diagram). The observation of three resonances for a system with a broad but smooth and monomodal particle-size distribution is surprising, since simple ferromagnetic resonance theory predicts one uniform precession mode.

However, for systems with an inhomogeneous magnetization, as expected for well-faceted nanocrystals with a large lattice mismatch at the particle–support interface,^[14] the excitation of other spin states becomes possible.^[15,16] The high-field resonance, whose position strongly depends on gas adsorption, can be attributed to a surface mode, which is very sensitive to changes in the boundary conditions at the surface of the particle. The intensity of this resonance decreases strongly if the orientation of the static magnetic field deviates from the perpendicular orientation with respect to the surface. The two other modes behave as conventional uniform precession modes. Both show a smooth variation of the resonance position with the angle of the incident static magnetic field (data not shown). An analysis of the angle dependence indicates an additional anisotropy component, which can be assigned to interface contributions. The lack of sensitivity of the resonance position to changes at the metal–vacuum interface (e.g. molecular adsorption or metal oxidation) indicates that the particle–substrate interface is the origin of this extra contribution. The temperature dependence of the signal corroborates this assignment, which also agrees with earlier studies with thin Ni films on metals.^[11] The splitting of the resonance into two lines may be a consequence of the uniaxial distortion of the nickel lattice along the (110) direction of the α -Al₂O₃ (1120) surface.

The particle–substrate interface plays an important role for the understanding of deposited-metal systems. The situation is complicated by the fact that this interface can rarely be described as a static system, especially at elevated temperatures and under reactive conditions. In the following we will show that magnetic properties can be used to monitor the interface reaction between an Al₂O₃ surface and Co and Ni particles at elevated temperatures.

Co (2 Å) was deposited at room temperature on a thin Al₂O₃ film grown on a NiAl(110) surface. The normalized intensity of the FMR spectra measured for this system was used as the reference (where the red curve crosses the y axis in Figure 3). Subsequently, the Co particles were oxidized with 30 L of oxygen at 300 K, resulting in complete loss of the FMR signal. Upon heating to 530 K the signal intensity was restored to 55% of its original value. As indicated by the scanning tunneling microscopy (STM) images taken under identical conditions, this procedure does not alter the morphology of the particles to a measurable extent. Upon repeating the procedure several times, the recovery of the FMR intensity decreased for subsequent cycles, indicating that the process becomes less effective. Based on this observation and the STM result, a simple thermal decomposition of the oxide phase can be ruled out. The observation can be explained by assuming that annealing to 530 K leads to a reduction of the Co oxide phase to metallic Co, caused by a concomitant oxidation of the NiAl substrate. The oxidation of NiAl increases the thickness of the alumina film progressively; similar results were obtained for Pd particles.^[17] This factor limits, most likely because of kinetic effects, the efficiency of the redox process, thus explaining the progressive drop of efficiency for subsequent cycles.

This type of solid-state reaction is not restricted to thin films. A similar effect was observed on an α -Al₂O₃ single

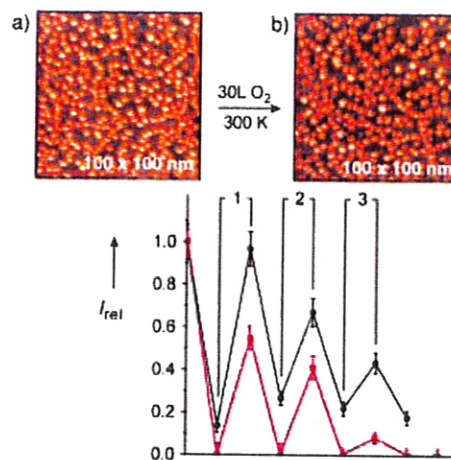


Figure 3. Top: STM pictures for 2-Å Co deposited at 300 K on a thin alumina film on NiAl(110):^[21] a) pristine deposits, b) after oxidation with 30 L of oxygen at 300 K. Diagram: Intensity of the FMR signals during the oxidation–heating cycles (see text). Black trace: 4-Å Ni deposited at 300 K on a (12×4) reconstructed α -Al₂O₃ (1120) surface and subsequently annealed to 900 K; red trace: 2-Å Co deposited at 300 K on a thin alumina film on NiAl(110).

crystal. Ni (4 Å) was deposited at 300 K on the reconstructed (12×4) α -Al₂O₃ (1120) surface and subsequently annealed to 900 K. The intensity observed after oxidation with 300 L of oxygen at room temperature and subsequent annealing to 900 K is shown in Figure 3 (black trace). The FMR intensity exhibits the same oscillatory behavior observed for the thin film. In this case the α -Al₂O₃ single crystal acts as a reducing agent because the reconstructed surface suffers from an oxygen deficiency in the top layers.^[18] However, the reduction capacity of the surface is limited because of the restriction of the oxygen deficiency to the few top layers, which explains the strong decrease in the efficiency of this process after several cycles.

In summary, we have shown that the magnetic properties of supported nanoparticles can be used to probe changes in the structure as well as the chemical environment of the particles. This has been demonstrated not only for adsorption and reaction with molecules from the gas phase but also for a reaction at the metal–support interface. Although all experiments described herein were carried out under UHV conditions, it is also possible to work at ambient pressure with FMR and ESR spectroscopy. The latter has been utilized for in situ model studies of Ziegler–Natta catalysts.^[19]

Experimental Section

The FMR experiments were carried out in a specially designed UHV apparatus, which has been previously described.^[20] The spectra were recorded with a commercial EPR spectrometer (Bruker, B-ER 420), which had been modified with an improved microwave bridge (Bruker, ECS041XK) and a new lock-in amplifier (Bruker, ER023M) to improve the signal-to-noise ratio. A commercial electron beam evaporator (EFM3 Focus/Omicron) was used to deposit the metals. A deposition rate of 1 Å min^{−1}, as calibrated by a quartz microbalance, was used for all experiments. The sample was biased to the voltage of the evaporation material to avoid an

acceleration of metal ions onto the surface. The pressure during metal evaporation never rose above 1.5×10^{-10} mbar, and the base pressure in the apparatus was better than 5×10^{-11} mbar. The coverage is given as an average height of a hypothetical, homogeneous film. Clean (1×1) and (12×4) reconstructed α - Al_2O_3 (11 $\bar{2}$ 0) surfaces (Crystec GmbH and Crystal GmbH, both Berlin) were prepared by annealing the sample several times for 20 min to 1200 K and 1500 K, respectively. The clean surface showed neither carbon nor other impurities within the sensitivity of Auger spectroscopy. The reconstruction of the surface after this treatment was verified by low-energy electron diffraction (LEED). The thin alumina film on the NiAl(110) single-crystal surface was prepared according to a procedure described in the literature.^[8]

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