Nanoparticle Restructuring in Heterogeneous Catalysis: Effect of Particle Size and Reactant

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Abstract:

Single-crystal surfaces, and later more complex model catalyst systems have laid the scientific basis for understanding the concept of structure sensitivity[1]. In this work, however, we employ a non-model study on a range of well-defined silica-supported Ni nanoparticle catalysts to understand the role of particle size dependent surface restructuring during several different catalytic reactions, and under working conditions. By use of a range of advanced in-situ and operando spectroscopic methods and á posteriori data analysis techniques, kinetic parameters regarding *catalytic* restructuring are described and distinguished from thermal restructuring. Reactant-induced and -dependent metal bond contraction and expansion mimics the “breathing” in nanoparticles, e.g. in the order ethene>>CO_2, and allows for active site quantification. From these results combined we hypothesize the existence of two types of structure insensitivity; apparent structure insensitivity and true structure insensitivity, which is onset by surface restructuring.

Keywords: Restructuring, Structure sensitivity, Hydrogenation, Active site

1. Introduction

Investigations of model systems, mainly single crystal facets, have been elemental in our current understanding of structure (in)sensitivity. However, mechanisms behind many classic structure (in)sensitive reactions, such as olefin hydrogenation, are still not entirely understood. For example, adsorbate induced dynamic restructuring of single crystal facets was found to be at the timescale of chemisorption and catalytic reactions in cornerstone work by Somorjai and co-workers in the early 1990’s[2]. However still, the influence of (surface) restructuring on non-model catalysts and under working conditions is not well understood. In this work, we employ a non-model study on a range of well-defined silica-supported Ni nanoparticle catalysts to investigate the role of particle size dependent surface restructuring during catalytic reactions.

2. Experimental

In this work, we have aimed to understand the role of surface restructuring in non-model catalysts and under working catalytic conditions. To enable this, we make use of a unique set of well-defined silica supported Ni catalysts with mean Ni diameters of 1.2-6.0 nm, and investigate them under a number of gas flows and different hydrogenation reactions (e.g. acetylene, ethylene, CO_2, and the hydrogenation reactions thereof). These systems are studied by a number of operando analysis techniques (FT-IR, and X-ray absorption spectroscopy with ms time resolution), in-situ analysis techniques (STEM-EELS, STEM-EDX) and advanced data analysis methods (i.e., multivariate analysis, modulation excitation, and phase sensitive detection).

3. Results and discussion

While classic structure insensitive reactions (e.g. ethene hydrogenation) show typical structure insensitivity patterns in catalytic testing and in FT-IR, XAS counterintuitively shows a large degree of restructuring during ethene hydrogenation (Figure 1a-e). However, for CO_2 hydrogenation (a classic structure sensitive reaction) the exact opposite is seen. In olefin hydrogenation, alkylidyne intermediates restructure the surfaces of Ni nanoparticles to an overall magnitude that is independent of their particle size. While in CO_2 hydrogenation this surface restructuring of studied nanoparticles shows a large extent of particle size dependence. Modulation excitation shows the presence of a multi-step active pathway in ethene hydrogenation for particle sizes larger than 2.5-3 nm, which suggests that nanoparticle restructuring is a prelude to activity in larger Ni particle sizes.

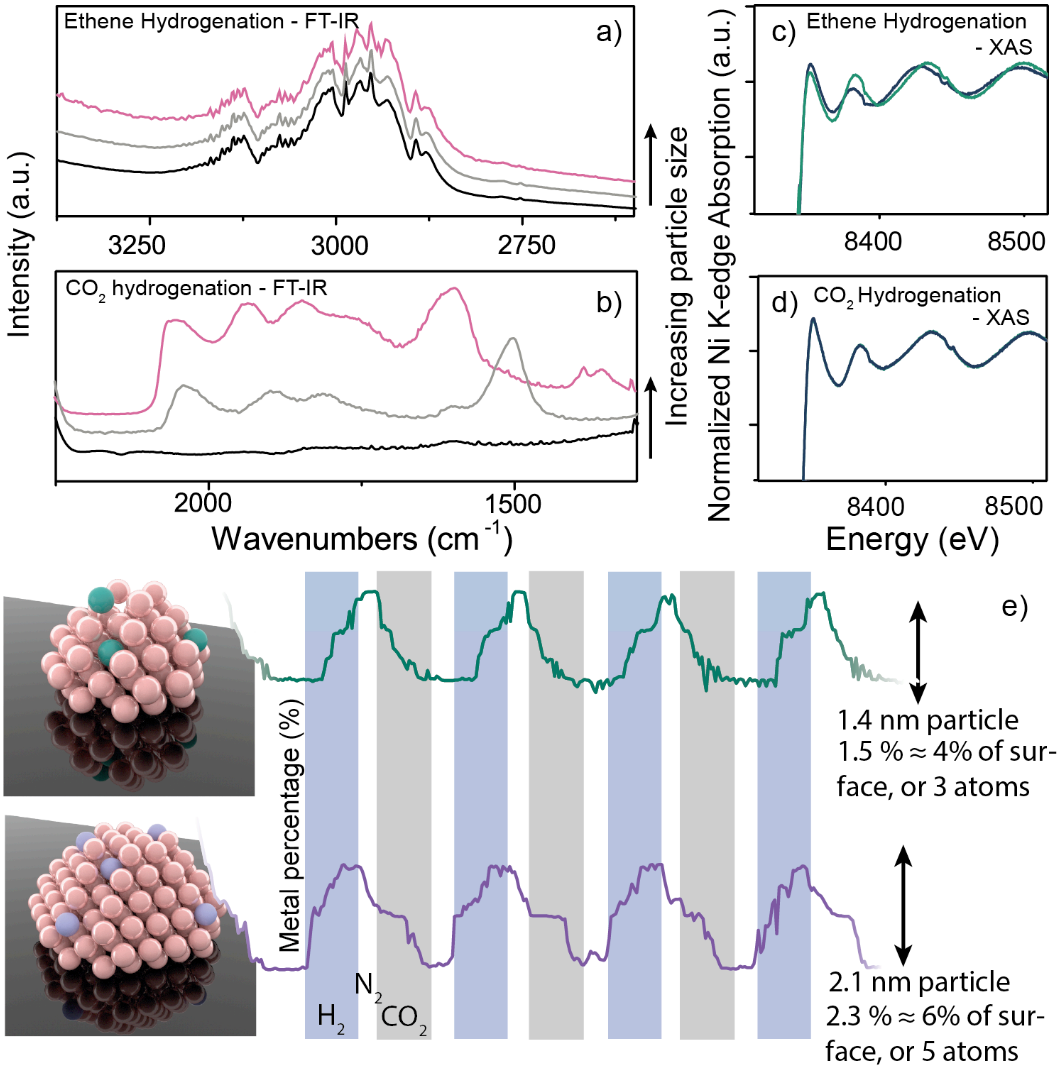

Figure 1. Operando FT-IR: spectra during ethylene hydrogenation at 150°C (a), and for CO_2 hydrogenation at 400°C (b). **Operando Q-XAS:** Ni nanoparticles supported on silica with mean diameter of 1.2 nm. Spectra of 1 nickel catalyst sample binned 200x in time (i.e. 30 s time resolution), during CO_2/H_2 modulation excitation (c) and ethene/H_2 modulation excitation (d) both conducted at 350°C (e) quantification of participating surface sites in CO_2 hydrogenation as an example.

4. Conclusions

Coordination numbers (determined by operando quick-XAS) as a function of time indicate severe restructuring induced by catalytic reactions with increasing chemisorption energy of reactants and intermediates. The specific contraction and expansion of real nanoparticular catalysts, under several different catalytic reactions and reaction conditions is captured for the first time using high time resolution operando XAS and the application of further developed data analysis techniques. We hypothesize the existence of two types of structure insensitivity; apparent structure insensitivity and true structure insensitivity, which is onset by surface restructuring. The results obtained suggest that any non-dynamic surface energy-minimized model for nanoparticle configurations will never yield fully accurate results in describing real catalysts under working conditions; and hence it underlines the importance of conducting operando spectroscopy investigations on non-model systems to understand basic concepts in catalysis.

References

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