Available online at www.sciencedirect.com

ScienceDirect

Surface Science Reports 70 (2015) 135–187

surface science reports

www.elsevier.com/locate/surfrep

Nanocatalysis: size- and shape-dependent chemisorption and catalytic reactivity

Beatriz Roldan Cuenya[a,*], Farzad Behafarid[b]

[a] *Department of Physics, Ruhr University Bochum, Bochum 44801, Germany*
[b] *Department of Physics, University of Central Florida, Orlando, FL 32816, USA*

Received 29 September 2014; received in revised form 31 December 2014; accepted 6 January 2015

Abstract

In recent years, the field of catalysis has experienced an astonishing transformation, driven in part by more demanding environmental standards and critical societal and industrial needs such as the search for alternative energy sources. Thanks to the advent of nanotechnology, major steps have been made towards the rational design of novel catalysts. Striking new catalytic properties, including greatly enhanced reactivities and selectivities, have been reported for nanoparticle (NP) catalysts as compared to their bulk counterparts. However, in order to harness the power of these nanocatalysts, a detailed understanding of the origin of their enhanced performance is needed. The present review focuses on the role of the NP size and shape on chemisorption and catalytic performance. Since homogeneity in NP size and shape is a prerequisite for the understanding of structure–reactivity correlations, we first review different synthesis methods that result in narrow NP size distributions and shape controlled NPs. Next, size-dependent phenomena which influence the chemical reactivity of NPs, including quantum size-effects and the presence of under-coordinated surface atoms are examined. The effect of the NP shape on catalytic performance is discussed and explained based on the existence of different atomic structures on the NP surface with distinct chemisorption properties. The influence of additional factors, such as the oxidation state of the NPs and NP–support interactions, is also considered in the frame of the size- and shape-dependency that these phenomena present. Ultimately, our review highlights the importance of achieving a systematic understanding of the factors that control the activity and selectivity of a catalyst in order to avoid trial and error methods in the rational design of the new generation of nanocatalysts with properties tunable at the atomic level.

Contents

Abbreviations: AFM, atomic force microscopy; BCC, body centered cubic; BE, binding energy; CN, coordination number; DRIFTS, diffuse reflectance infrared spectroscopy; DFT, density functional theory; DMF, dimethylformamide; EXAFS, extended X-ray absorption fine-structure spectroscopy; E-TEM, environmental transmission electron microscopy; FCC, face centered cubic; FTIR, Fourier transform infrared spectroscopy; GISAXS, grazing-incidence small-angle X-ray scattering; HAADF-STEM, high-angle annular dark-field scanning transmission electron microscopy; HOPG, highly oriented pyrolytic graphite; HRTEM, high resolution transmission electron microscopy; HXRD, hard X-Ray diffraction; CID, chemical interface damping; IRAS, infrared reflection absorption spectroscopy; ITO, indium tin oxide; KMC, kinetic Monte Carlo; L, Langmuir; LEIS, low energy ion scattering; L–H, Langmuir–Hinshelwood; LSPR, localized surface plasmon resonance; ML, mono-layer; MD, molecular dynamics; MVK, Mars–van Krevelen; NP, nanoparticle; PVP, poly (vinyl pyrrolidone); P2VP, poly-2(vinyl pyrrolidone); QMS, quadrupole mass spectrometer; RT, room temperature; SCAC, single crystal adsorption calorimetry; SFG, sum frequency generation; SMSI, strong metal-support interaction; STO, strontium titanate, $SrTiO_3$; STM, scanning tunneling microscopy; STS, scanning tunneling spectroscopy; SXRD, surface X-Ray diffraction; TEM, transmission electron microscopy; TOF, turnover frequency; TPD, temperature programmed desorption; TPR, temperature programmed reduction; XANES, X-ray absorption near-edge spectroscopy; XAS, X-ray absorption spectroscopy; XPS, X-ray photoelectron spectroscopy; XRD, X-ray diffraction; VOC, volatile organic compounds; WBDF, weak beam dark field

[*] Corresponding author.
E-mail address: Beatriz.Roldan@rub.de (B. Roldan Cuenya).

http://dx.doi.org/10.1016/j.surfrep.2015.01.001
0167-5729/

---

1. Introduction

Unraveling the complex interaction between catalysts and reactants and tailoring their chemical reactivity at the atomic level are key steps towards gaining fundamental insight in catalysis. Such knowledge could enable the rational design of the next generation of highly active, selective, and stable nanosized catalysts for industrial applications. Consequently, intense effort has been exerted towards understanding the properties that affect the catalytic performance of metal nanoparticles (NPs) such as their size and shape [1–9], interaction with the support [10–13], and oxidation state [14–16]. In order to deconvolute the influence of each of these NP properties on catalyst reactivity, model systems with highly tunable structure must be synthesized and tested under controlled environments.

Arguably, the most important property to understand is the influence of NP morphology on catalytic ability. NP size and in particular shape will determine the availability of certain active facets or low coordinated sites on the NP surface, which can affect the binding strength of reactants and intermediates and thereby the activity and selectivity of a particular reaction. In addition, NP morphology will affect the degree of interaction of the metal with the support, influencing charge transfer phenomena or the extent of interfacial strain. While size control has been readily achieved for nanocatalysts, shape control, particularly for NPs below 10 nm, has been much more challenging. However, new synthesis methods have allowed progress in this area [9].

Further complexity is added to understanding the origin of NP catalytic properties when catalysts are considered under realistic reaction environments. NPs which are carefully synthesized with well-defined size and shape may evolve in morphology during a reaction in response to elevated temperatures or the chemisorption of gas molecules [17–19], meaning that structural and chemical characterization which is performed before and after a reaction may not reflect the actual state of the catalyst during the reaction. Consequently, *in situ* and *operando* measurement techniques that can bridge this pressure gap have become increasingly important to understanding the dynamic nature of active NP catalysts and their response to their environment [20,21].

This review article focuses on correlating the catalytic reactivity of NPs and their geometry. It will be illustrated that chemisorption and catalytic properties such as the onset reaction temperature, the activity, and selectivity of a nanocatalyst may be tuned through controlled synthesis of NPs with well-defined sizes and shapes.

2. Synthesis methods resulting in size- and shape-selected nanostructures

In order to understand and further harvest the potential novel chemical properties of nanostructured materials in the field of catalysis, significant effort needs to be made in the years to come towards the synthesis of structurally well-defined systems, including size- and shape-selected nanoparticles. A variety of approaches have been used in the past for the synthesis of nanoparticles, such as thermal evaporation in vacuum [22–27], atomic layer deposition [28–31], electron-beam lithography [32–35], nanosphere lithography [35–39], pulsed laser deposition [34,40,41], buffer-layer assisted growth [42–44], chemical vapor deposition [45–47], gas condensation, ionized cluster beam deposition [48–52], electrochemical deposition [53–57], sol–gel or colloidal techniques [58–60], deposition–precipitation and impregnation methods [6,61,62], molecular cluster precursors [63], or solvothermal synthesis [64–66].

Nevertheless, only a few of the above methods are suitable for the growth of nanostructures with controlled size and shape