

Nanoparticle Exsolution on Perovskite-Based Catalysts

Subjects: Physical Chemistry

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Definition

In heterogeneous catalysis, surfaces decorated with uniformly dispersed, catalytically-active (nano)particles are a key requirement for excellent performance. Besides standard catalyst preparation routines—with limitations in controlling catalyst surface structure (i.e., particle size distribution or dispersion)—exsolution is a potential novel and time efficient route to precisely tailor catalyst surface morphology and composition of perovskites:

Perovskite-type oxides of nominal composition ABO_3 with transition metal cations on the B-site can exsolve the B-site transition metal upon controlled reduction. In this exsolution process, the transition metal emerges from the oxide lattice and migrates to the surface where it forms catalytically active nanoparticles. Doping the B-site with reducible and catalytically highly active elements, offers the opportunity of tailoring properties of exsolution catalysts.

1. Introduction

In heterogeneous catalysis, controllable surface properties and a maximum amount of stable uniformly-dispersed catalytically highly active sites on the surface of a porous material are of key importance. Typically, catalysts consist of metal, alloy, or oxide nanoparticles embedded in an oxide support material. Depending on the type of catalytic reaction, active sites are either just nanoparticles themselves or the combination of nanoparticles and oxide support. Ideally, catalysts exhibit long-term stability and activity during reaction. Therefore, resistance to catalyst poisons, inhibition of carbon deposition (blocking of active sites), and prevention of particle agglomeration and sintering (loss of active surface area) is essential.

Typically, these structures are prepared by deposition, impregnation or precipitation techniques^{[1][2]} followed by catalyst activation prior to reactions via oxidation and reduction^[3]. Although these approaches are applied widely, they offer limited control over size, distribution, and anchorage of deposited species, not only during preparation but also during catalyst activation or operation, and they might be time consuming and costly^[4].

Alternatively, an emerging concept is to grow the nanoparticles in situ, by reduction or during catalytic reaction, directly from the (porous) oxide backbone support itself^{[4][5][6]}. Perovskites (nominal composition ABO_3 with A and B being a large and small cation, respectively, cf. Figure 1a) can incorporate catalytically highly active elements as cations on the B-site of the perovskite lattice (e.g., Ni^{[4][7]}, Fe^{[4][8]}, Co^[9], Cu^{[4][9]}, Pt^[10], Pd^{[10][11]}). Upon exposure to reducing conditions, these elements can be partly exsolved as nanoparticles, thus opening the possibility of in situ growth of active catalysts^[12], see sketch in Figure 1b. In comparison to traditional deposition techniques, this process produces finer and higher dispersed catalyst nanoparticles^{[4][13][14]} and is more time- and cost-effective, as it does not require multiple "deposition" steps or expensive precursors^[15]. Furthermore, it has been shown that nanoparticles formed by exsolution exhibit improved sintering stability during catalytic reaction^[16]. In addition, due to a possible reversibility of the nanoparticle exsolution process, particle agglomeration can be avoided by reoxidation cycles^[17], hence, greatly enhancing the catalyst lifetime^{[12][18]}.

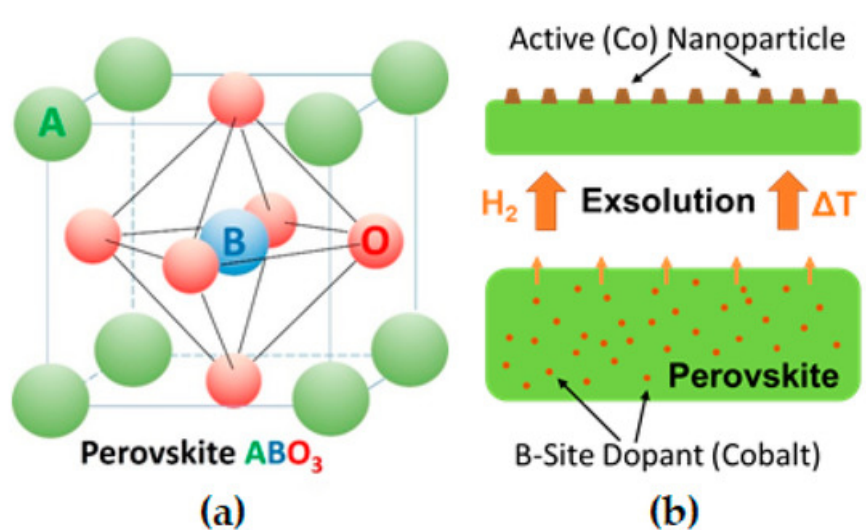


Figure 1. (a) Perovskite lattice structure; (b) simplified exsolution process.

Mechanisms for nanoparticle exsolution from perovskites were investigated already by multiple groups⁴[11][19][20][21]. It is generally accepted that exsolution catalysts need easily reducible dopant cations²², such as Ru, Co, Pd, or Ni²³, that will form metallic deposits on the perovskite surface. Thus, depending on temperature and oxygen chemical potential in the gas phase (i.e., the strength of reduction), dopants and in some cases also lattice cations are reduced and exsolved as nanoparticles⁸[24]. As an explanation for exsolution mechanisms, Neagu et al!⁴ proposed that oxygen vacancies created by reduction destabilize the perovskite lattice, especially when their concentration is high and when additionally A-site cation vacancies are present. Such combined oxygen and A-site cation vacancy formations may locally cause spontaneous exsolution of B-site species in an attempt to re-establish stoichiometry across all sites. Oh et al.¹⁹ implied that the morphological evolution of nanoparticles could be explained using a simple energy-based model, which accounts for interplay between surface free energy and strain energy induced by the included metal nucleate. By quantitative strain field modelling, they could demonstrate that this provides the driving force for exsolution processes. Similarly, Han and co-workers applied classical nucleation theory to the exsolution process and found the strain between metal particle and supporting oxide being a potential influencing factor for the particle size.

2. Conclusion

Usually, formation of nanoparticles on the surface is accomplished via a reductive treatment. For example, Arrivé et al.²⁵ showed for Ni doped $LaSrTiO_3$ that pre-reduction in H_2 at 1573 K leads to exsolution of Ni particles on the surface of solid oxide electrochemical cells leading to improved electrochemical performance. Additionally, Papargyriou and Irvine demonstrated Ni exsolution from Ni-doped $La_{0.75}Sr_{0.25}Cr_{0.5}Fe_{0.5}O_3$ perovskite by H_2 reduction¹⁴. Nanoparticles with a size of 30–50 nm were formed on the surface, leading to an improvement of catalytic properties of the material. Similarly, Sun et al.¹³ could observe Ni nanoparticle exsolution from Ni-doped $La_{0.7}Sr_{0.3}CrO_3$ upon pre-reduction in H_2 . Most of the recent studies on exsolution phenomena are reported and studied by the electrochemical community (mainly with respect to fuel cell technology), but utilization of this effect for preparing tailored heterogeneous catalyst materials is still rare—even though the initial idea came indeed from the catalysis community¹².

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Keywords

Exsolution; Nanoparticles; Perovskites; Tailored Surfaces

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