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Single-site zinc on silica catalysts for propylene hydrogenation and propane dehydrogenation: Synthesis and reactivity evaluation using an integrated atomic layer deposition-catalysis instrument

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ABSTRACT

Alkyl-zinc and zinc oxide-type sites were synthesized via atomic layer deposition on high-surface-area silica using an integrated atomic layer deposition-catalysis instrument (I-ALD-CAT). One-cycle ALD experiments using diethylzinc (DEZ) afforded Zn/SiO_2 systems that provided key insights into the reactivity and stability of Zn sites as a function of dispersion at the submonolayer level. The I-ALD-CAT tool design allowed for systematic comparison of the reactivity of different grafted zinc sites. Open-shell 16-electron, tricoordinate ethyl zinc-silica sites exhibit higher activity in propane hydrogenation-dehydrogenation compared to 18-electron, tetracoordinate zinc oxide-type centers. Silica surface saturation with Zn(II) sites (~75% of a monolayer) results in facile zinc agglomeration and catalyst deactivation under reaction conditions. Reduced DEZ dosing coupled with thermal substrate pretreatment techniques (e.g., dehydration under vacuum) resulted in increased Zn dispersion and produced Zn/SiO_2 catalysts with improved activity and stability under propylene hydrogenation (200 °C) and propane dehydrogenation (550 °C) conditions.

1. Introduction

Single-site heterogeneous catalysis remains a rapidly growing area due to its potential to combine the tunability of molecular catalysts with the stability of heterogeneous materials under a range of process conditions (e.g., temperature, pressure, solvent) [1,2]. Systematic investigation of active site formation during synthesis and the transformations these species and reactive intermediates undergo during catalysis can harness key structural and mechanistic insights that are essential for the purposeful design of robust single-site catalysts with improved efficiency. However, systematic study of the transformations that these isolated sites undergo remains challenging due to the limitations of the synthesis procedures (e.g., formation of a distribution of sites), and the difficulty in handling sensitive catalytic species and intermediates from synthesis to the reactivity testing stage. Ideally, strategies integrating high-precision active site synthesis methods with immediate catalyst performance testing could allow for the systematic investigation of the catalytic properties of these supported sites without material decomposition from air- or moisture exposure.

In order to prepare single-site catalysts that are uniform in function, they must be synthesized using atomic-level control [3,4]. Recent advances in synthesis techniques have produced catalytic materials with much improved activity, selectivity and stability [5–9]. One thing all of these synthesis methods (e.g., impregnation, ion-exchange, precipitation, organometallic grafting) still lack in many cases is control of the structure, producing materials with a distribution of active sites, which in turn impacts performance. In principle, **A**tomic **L**ayer **D**eposition (ALD) is a high-precision grafting technique that can synthesize a variety of supported catalytic sites (e.g., single atoms or clusters) at the atomic/monolayer level [3,10,11]. ALD is a vapor-phase grafting

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method that relies on a stoichiometric and thus self-limiting reaction of chemical precursors with substrate surface functionalities [5–12]. The self-limiting nature of the ALD process presents a number of synthetic advantages that include (1) uniform active site dispersion, (2) high conformity to surface features which, in certain cases, allows for maximum utilization of the support surface area, and (3) high level of reproducibility [3].

Although ALD as a catalyst synthesis tool has been applied mainly for the controlled synthesis of supported bulk – *nanoscale in size* – structures such as metal particles [13], films [14], alloys [15] and core-shell nanoparticles [16], it comprises an ideal strategy for accessing supported single-site catalysts since *the initial nucleation of sites during ALD should consist of isolated sites.* So far, only a few reports of ALD for single-atom catalysts have appeared [17]. Hence, improved understanding of synthesis mechanisms and optimization of key factors for the design of effective ALD synthesis methods to access single sites is warranted.

Our group recently reported the synthesis of isolated, low-coordinate Zn(II) sites on silica via strong electrostatic adsorption. These sites were shown active toward propylene hydrogenation (200 °C) and selective propane dehydrogenation (550 °C). Computational studies revealed the involvement of tricoordinate Zn(II) sites and an alkyl-zinc intermediate in the catalytic cycle (Fig. 1). However, systematic comparison of the intrinsic reactivity of these intermediates remains challenging due to difficulties in the synthesis, and the inherent instability of the species on oxide supports.

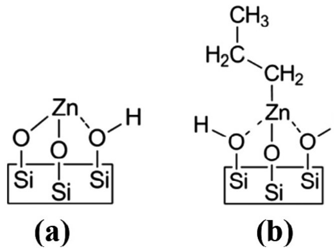

Fig. 1. Proposed reactive intermediates for a previously reported single-site Zn(II)/SiO_2 catalyst for propylene hydrogenation and propane dehydrogenation: (a) three-coordinate Zn(II) site and (b) alkyl-zinc species.

In this paper, we report the use of an **I**ntegrated **A**tomic **L**ayer **D**eposition-**Cat**alysis (I-ALD-CAT, Fig. 2) [18] synthesis and catalyst reaction testing tool for the synthesis of isolated alkyl-zinc and zinc oxide-type sites via one-cycle ALD methods and immediate *in situ* evaluation of the reactivity of these sites at the atomic-scale/submonolayer level under propylene hydrogenation and propane dehydrogenation conditions [18]. The I-ALD-CAT tool – *the first of its kind* – has the capability of (1) ALD synthesis on a support loaded into a plug-flow reactor, a design element that allows for (2) immediate *in situ* catalyst performance evaluation under plug-flow conditions *without material exposure to air or moisture* (Fig. 2).

The approach presented in this report provides key insights into the mechanism of zinc grafting on hydroxylated supports, and the reactivity and stability of these alkyl-zinc and zinc oxide-type sites as a function of zinc dispersion and nuclearity. Additionally, this study presents the use of an organo-zinc pre-catalyst where the initial pre-catalyst ligand (ethyl, C2) is well differentiated from the reacting alkene/alkane (propylene and propene, both C3 species). This approach allowed for the unambiguous monitoring of the activation pathways that the pre-catalyst undergoes during catalysis. Based on this understanding, optimized synthesis of Zn/SiO_2 catalysts with improved activity and stability have been achieved by ALD.

2. Experimental section

2.1. General ALD synthesis conditions

Silica (SiO_2, Davisil 646, 40–50 mesh, 300 m^2/g (BET surface area) and 1.1 cc/g, Sigma-Aldrich) was used as substrate for the gas-phase grafting of Zn catalysts. The synthesis was performed using an ARRADIANCE Integrated ALD-Catalysis tool (model ARR-100000 GEMSTAR-CAT Dual System). A series of ALD experiments were carried out to ensure the self-limiting nature of the gas-phase deposition reaction (see details in the Supporting Information). 160–320 mg of SiO_2 was loaded into a 406 mm × 7 mm (i.d.) stainless steel, plug-flow tube reactor. Unless otherwise stated, the silica substrate for each ALD synthesis experiment was purged with N_2 (10 sccm) for 30 min after reactor tube installation, and subsequently heated at 200 °C for 1 h under vacuum (0.1 Torr). (Note:

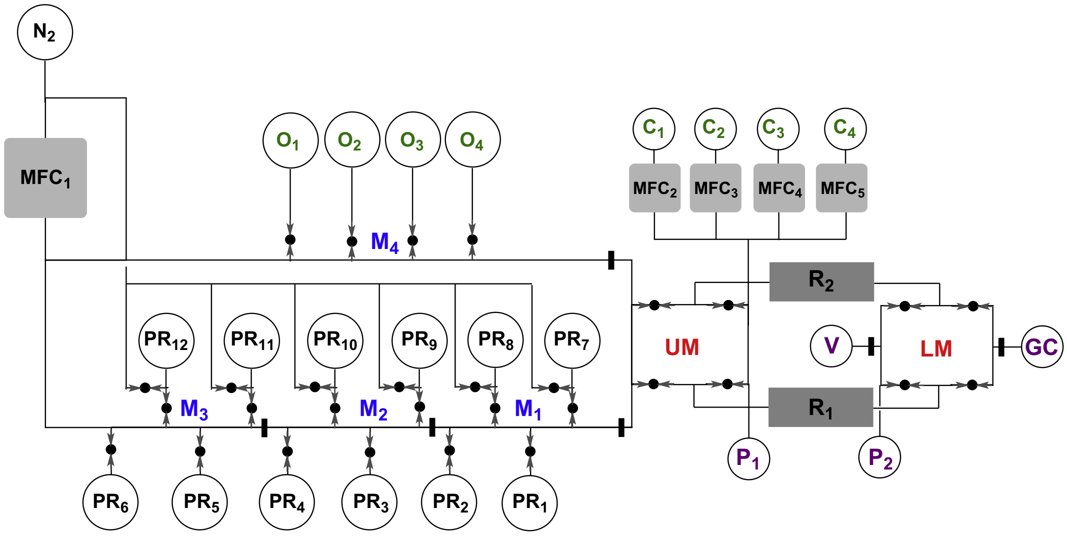

Fig. 2. Schematic diagram for the I-ALD-CAT tool. Lower left: Metal precursors (PR_1–PR_{12}). Upper left: Oxidizing/reducing reagents (O_1–O_4). Upper right: Catalysis reagents (C_1–C_4). Middle right: Plug-flow reactors (R_1, R_2). Middle far-right: Product manifold (LM). The I-ALD-CAT has the capability of providing gaseous reagents comprised of 12 different ALD precursors, 4 oxidizing or reducing agents, and 4 catalytic reaction feeds to the two plug-flow reactors. The reactor is able to immediately test these single site catalysts (or any newly synthesized materials) on a wide range of reactions and process conditions. Volatile products of the ALD synthesis and catalytic reactions can be analyzed by both GC and mass spectrometry [18].