

Development of activity–descriptor relationships for supported metal ion hydrogenation catalysts on silica

Cong Liu^{a,*}, Jeffrey Camacho-Bunquin^a, Magali Ferrandon^a, Aditya Savara^b, Hyuntae Sohn^a, Dali Yang^a, David M. Kaphan^a, Ryan R. Langeslay^a, Patricia A. Ignacio-de Leon^c, Shengsi Liu^d, Ujjal Das^e, Bing Yang^{a,f}, Adam S. Hock^{a,g}, Peter C. Stair^{a,d}, Larry A. Curtiss^e, Massimiliano Delferro^{a,*}

^a Chemical Sciences and Engineering Division, Argonne National Laboratory, Lemont, IL 60439, USA

^b Chemical Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830, USA

^c Energy Systems Division, Argonne National Laboratory, Lemont, IL 60439, USA

^d Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

^e Materials Science Division, Argonne National Laboratory, Lemont, IL 60439, USA

^f Energy Research Resources Division, Dalian Institute of Chemical Physics, Dalian 116023, China

^g Department of Chemistry, Illinois Institute of Technology, Chicago, IL 60616, USA

ARTICLE INFO

Article history:

Received 30 March 2018

Accepted 3 June 2018

Available online 15 June 2018

Keywords:

Hydrogenation

Metal ion

DFT

Activity descriptor

Silica

ABSTRACT

Single-site heterogeneous catalysts receive increasing attention due to their unique catalytic properties and well-defined active sites. We report a combined computational and experimental study on a series of silica-supported metal ion hydrogenation catalysts (i.e., In^{3+} , Ga^{3+} , Zn^{2+} , Mn^{2+} , and $\text{Ti}^{4+}/\text{SiO}_2$). These catalysts were synthesized, characterized, and evaluated for gas-phase propylene hydrogenation. Computational studies were carried out on active-site structures and reaction mechanisms. An activity–descriptor relationship was established, which correlates a computational quantity (reaction free energy of the metal hydride formation) with the experimental reaction rate, as a function of the metal. Microkinetic modeling provided qualitative kinetic insights into the activity–descriptor relationship. This relationship was used to predict the trend of activities in a variety of M/SiO_2 catalysts. These fundamental studies and the developed activity–descriptor relationship open up new opportunities for rational design of hydrogenation catalysts.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Single-site heterogeneous catalysts (SSHCs), defined as “a catalyst constituted by a metal atom, ion, or small cluster of atoms, held by surface ligands to a rigid framework” [1–3], have gained increased attention as they possess the desirable properties of both homogeneous and heterogeneous catalysts. In addition to their high reactivity, selectivity and recyclability, the well-defined sites in SSHCs also allow for systematic structure–function correlations that may be useful in the design of more efficient catalysts [1,4–8]. Examples of SSHCs include, but are not limited to, supported organometallics [9–14], dispersed metal ions on oxides and zeolites [15,16], polymers [17–24], metal–organic frameworks [25–27], carbon based supports [28], and metal surfaces [29,30], etc. Among these SSHCs, the development of isolated metal ion catalysts on oxide supports remains limited by the availability of synthesis

methods with atomic-level control of active site formation. State-of-the-art synthesis techniques such as surface organometallic chemistry (SOMC) and strong electrostatic adsorption (SEA) [31], have become key-enabling tools in the synthesis of this class of SSHCs [4,32,33].

Amorphous silica (SiO_2) is widely used as a support material due to its high surface area, high thermal stability, and structural flexibility [24]. Moreover, it bonds rather readily to a large selection of elements in the periodic table [5,24]. Silica-supported SSHCs have shown great potential in various fundamental and industrially relevant chemical transformations such as hydrogenation/dehydrogenation [34–42], C–C coupling [43] olefin epoxidation [44], and polymerization [45–50]. Our group recently reported that some of these systems (e.g., $\text{Zn}^{2+}\text{-SiO}_2$, $\text{Ga}^{3+}\text{-SiO}_2$) are active for non-oxidative alkane dehydrogenation/olefin hydrogenation [34–42]. Given that SSHCs can be extended to a broad scope of potential materials, improved design strategies to access more active surface-supported isolated metal ions are necessary.

* Corresponding authors.

E-mail addresses: congliu@anl.gov (C. Liu), delferro@anl.gov (M. Delferro).

First-principles calculations can provide molecular understanding of the active-site structures and catalytic properties, and can also be used to establish activity–descriptor relationships to predict more active catalysts [51–55]. For example, activity–descriptor relationships have been successfully employed in developing solid-state electro-catalysts and organic photovoltaic (OPV) materials [51–56]. However, there remains a dearth of systematic and comprehensive theoretical studies/predictions for SSHCs [5–7,24,34,35,57–64]. With this motivation, we carried out an experiment and theory combined study on a series of silica-supported metal ion catalysts (M/SiO_2 , $M = \text{In}^{3+}$, Ga^{3+} , Zn^{2+} , Mn^{2+} and Ti^{4+} , these ions were neutralized by anionic SiO^- groups), using propylene hydrogenation as a probe reaction. Since olefin hydrogenation is the microscopic reverse of alkane dehydrogenation, an industrially relevant and challenging transformation, catalytic performance in hydrogenation reactions can provide useful insights into dehydrogenation intermediates and structure reactivity relationships while providing favorable thermodynamics under mild conditions [13d]. Both computations and experiments were carried out on these five catalysts to generate a detailed understanding of the active sites, catalytic activity and reaction mechanisms. Furthermore, a correlation between the initial hydrogenation rate and a critical activity descriptor was established (i.e., the activity–descriptor relationship). Microkinetic modeling provides a mechanistic understanding of this qualitative correlation. The activity–descriptor relationship developed then served to predict future possible directions for investigations of supported metal ions.

2. Experiment and simulation details

2.1. Synthesis and characterization of M/SiO_2

Detailed experimental sections are included in SI (Sections S1–S4). Briefly, the 2.7% (w/w) $\text{Ga}^{3+}/\text{SiO}_2$ [37] and 2.5% $\text{Zn}^{2+}/\text{SiO}_2$ catalysts [38] were synthesized using the procedures previously reported while the 3% $\text{Mn}^{2+}/\text{SiO}_2$ and 3% $\text{Ti}^{4+}/\text{SiO}_2$ systems were synthesized via surface organometallic chemistry with bis(mesityl)manganese(II) and tetrakis(isopropoxy)titanium(IV), respectively, in toluene [65]. The 5.5% In^{3+} sites were installed on SiO_2 using molecular InMe_3 precursor in pentane. Note that it is conceivable for various molecular precursors (e.g., metal alkoxide, metal aryl) to produce different pre-catalyst properties and formation (e.g., monomers vs dimers, presence/absence of highly reactive M–C groups). However, the synthetic protocols employed, as verified by a combination of characterization techniques, gave a series of pre-catalysts with a common structural feature: monodispersed cations on SiO_2 where the potentially catalytic element is stabilized by siloxy groups and, in certain cases, $\text{H}_2\text{O}/\text{OH}$ ligands

(See Sections S1, S2 and S4 for detailed characterization). In addition, we have established, unambiguously, the absence of metal–organic moieties (e.g., In–Me, Ga–In, Zn–Et, Mn–Mes, and Ti–O⁺Pr) that could provide alternative activation pathways/entries into a catalytic hydrogenation cycle.

2.2. Evaluation of M/SiO_2

The initial activity of propylene hydrogenations (15 min at each temperature of 150, 175 and 200 °C) was measured for each catalyst (Details see Section S3). Temperature above 200 °C were not taken into account due to catalyst deactivation. Long-term hydrogenation experiments (Fig. S20) revealed that Ga^{3+} [37,41], Zn^{2+} [35,38], and Mn^{2+} systems deactivate over time, suggesting a possible dynamic behavior of the catalyst structure. Since no steady-state hydrogenation rate can be obtained, it is important to note that only the initial TOF values were considered for the theory–experiment correlation as the initial hydrogenation rates are more attributable to the structure(s) of the (a) as-prepared pre-catalysts and (b) activated species elucidated via *ex situ* and *in situ* spectroscopic characterization.

2.3. Computational models

Amorphous silica is used as a support for monomeric metal ion species. Keeping the long-range structural order of the SiO_2 system is critical to model such an amorphous material. One approach is to apply periodic boundary conditions (PBCs) on slabs representing amorphous silica [60,66] or directly on amorphous silica structures obtained from molecular dynamics simulations [67]. However, the large number of metal ion species and configurations considered in the present work make PBC calculations practically challenging. Alternatively, we have adopted the approach of a cluster model with silsesquioxane cages to model silica. Previous studies have shown that silsesquioxane cages are good representations for amorphous silica [68]. The cluster model (Fig. 1) was developed in our recent computational study of SiO_2 supported metal ions [69]. This model contains six silica rings, four hydroxyls and the corner Si atoms were terminated with hydrogen atoms. It was previously shown to sufficiently reproduce the relative stability of the metal center species and the silica ring strain of the periodic model of silica [69]. Each metal ion is neutralized by the anionic Si–O groups in the cluster model (by removing protons in the model in Fig. 11). To further validate the model for the present work, we calculated the hydride formation reaction energy (Eq. (1)) on $\text{In}^{3+}/\text{SiO}_2$ site using both the cluster model and a periodic hydroxylated silica model (Section S5.1):

$$\Delta E_{M(H)-O(H)} = E_{M(H)-O(H)} - E_{M-O} - E_{H_2} \quad (1)$$

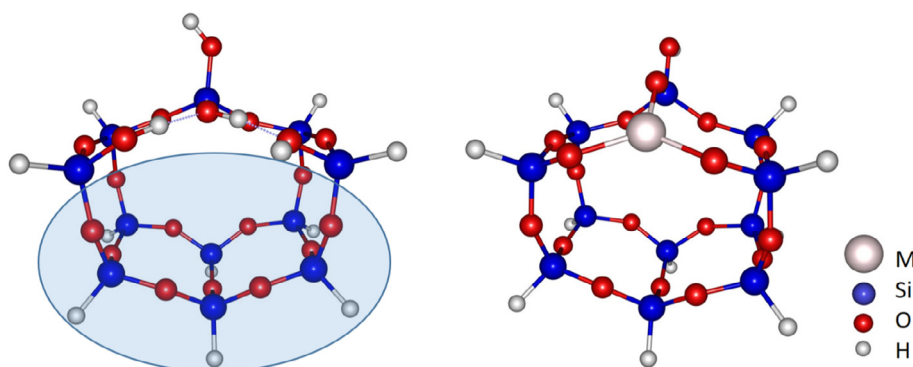


Fig. 1. Cluster models of hydroxylated silica and silica supported metal ion. The highlighted region is kept frozen during geometry optimization and frequency calculations for all the cluster models.

Download English Version:

<https://daneshyari.com/en/article/7762342>

Download Persian Version:

<https://daneshyari.com/article/7762342>

[Daneshyari.com](https://daneshyari.com)