



Investigation of inherent differences between oxide supports in heterogeneous catalysis in the absence of structural variations



Nuoya Yang^a, Stacey F. Bent^{b,*}

^a Department of Materials Science and Engineering, Stanford University, 496 Lomita Mall, Stanford, CA 94305, United States

^b Department of Chemical Engineering, Stanford University, 443 Via Ortega, Stanford, CA 94305, United States

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ABSTRACT

Oxide supports in heterogeneous catalysts can profoundly influence the catalytic properties of the metal or alloy active phase. Supports prepared by conventional methods can have not only different chemical properties but also different structural properties depending on the oxide. These structural differences can in turn affect the dispersion, distribution, and accessibility of the active phase. In this study, we apply an atomically-controlled synthesis method to isolate the effects arising from the different chemical properties of three oxide supports – titania, alumina and silica – used in Rh catalysts for syngas conversion reactions. We perform atomic layer deposition of titania and alumina to chemically modify the surface of silica gel, without changing its structural characteristics such as surface area and porosity. An inverse catalyst structure is also fabricated by depositing titania and alumina as overlayers onto silica-supported Rh. Titania is found to increase syngas conversion activity and higher hydrocarbon selectivity as both a support layer and an overlayer. An alumina support layer increases Rh nanoparticle dispersion and activity whereas an alumina overlayer decreases the activity of Rh. No significant increase in higher oxygenate selectivity was observed with either titania or alumina.

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1. Introduction

The support materials of heterogeneous catalysts exert a profound influence on the activity, selectivity and stability of the active metal, alloy or oxide species. Oxide supports can influence catalytic properties by changing the dispersion and shape of the active phase [1,2], affecting charge transfer [3,4], participating in the catalytic reaction [5–8], and forming new phases with the active metal through chemical interactions [3,9,10]. Understanding support effects is thus critical for choosing the appropriate support material and optimizing the overall catalytic properties. There are many aspects of the support that can impact the performance of heterogeneous catalysts, including its inherent chemical composition [4,11], reducibility [12,13], surface acidity [8,14,15], and structural properties. Structural properties such as surface area and porosity can also affect the spatial distribution of the active phase throughout the support, pressure drop during the reaction, and accessibility of the active phases to reactants [15–17]. Different oxides may have very different structural properties [18,19], which depend on both the nature of the material and the preparation

methods [20,21]. Finally, impurities inside the support materials, which often vary from batch to batch in commercial products, can contribute to changes in reactivity [22–25]. Such changes in structural characteristics and impurity profile inevitably become convoluted with the chemical properties of the support and obscure support effects originating from the chemical properties. The aim of this study was to introduce a robust synthetic strategy to investigate the inherent effects (chemical or electronic) of different oxide support materials on catalytic performance. This strategy allows separation of intrinsic effects from those secondary effects stemming from different structural or physical properties of the support.

In this study, we use atomic layer deposition (ALD) to introduce ultrathin layers of metal oxide onto silica gel in order to modify the chemical properties of the silica support surface without altering its structural characteristics. ALD, which is based on self-saturating reactions between vapor reactants and a solid surface, is chosen because it can achieve thin film deposition with Angstrom level control over the film thickness on high surface area, high aspect ratio substrate typical of catalyst supports [26,27]. Modification of the silica support by ALD can maintain the original porosity and surface area and avoid introducing impurities, which allows the chemical properties of the support surface to be changed without significantly changing its physical or structural

* Corresponding author.

E-mail addresses: nyyang@stanford.edu (N. Yang), sbent@stanford.edu (S.F. Bent).

properties. ALD has rapidly gained attention for application to the synthesis and modification of supported noble metal and transition metal catalysts [28–30]. Compared to conventional wet synthesis based methods, ALD can provide more accurate control over the catalyst composition and structure. ALD overcoating of metal oxides (e.g. Al_2O_3 , TiO_2 , SiO_2 and ZrO_2) on supported Pd [31–33], Au [34], Cu [35], and Co [36] nanoparticles has improved the stability of the catalysts against coking and sintering. Higher activity or selectivity toward desirable products has also been demonstrated on supported Pd [31,37] and Pt [38] catalysts with ALD metal oxide overcoating. Compared to the synthesis and overcoating of supported metal catalysts, the application of ALD in studying support effects has been much less explored.

This study focuses on a comparison between silica, alumina and titania supports on supported Rh catalysts for syngas conversion. Syngas conversion is a promising and versatile pathway to produce synthetic transportation fuels or other value-added chemicals from natural gas and renewable resources such as biomass, CO_2 and organic waste [39–42]. The support material can significantly change the selectivity pattern and the overall activity of Rh. Silica, alumina and titania are among the most commonly used support materials for Rh syngas conversion catalyst as well as other heterogeneous catalysts, due to their relatively inert chemical nature, high surface area, and superior stability [15]. Titania is a reducible oxide that may form encapsulation layers onto Rh under high temperature reduction [9], form partially reduced Ti cations which could participate in the reaction [43], or even form intermetallic compound with Rh [44]. Alumina is commonly considered to be an acidic support which has been reported to stabilize extremely small Rh nanoparticles [45]. Studies that directly compare the effects of these three commonly used supports are rare [18,46–48], with some earlier reports focused only on infrared studies [49–51] or CO dissociation and hydrogenation properties [52]. Discrepancies also exist regarding the impacts of these oxides on the syngas conversion activity and selectivity. Titania and alumina have been shown to lead to higher activity and increased methane selectivity than silica. On the contrary, it has also been reported that silica leads to higher methane selectivity while titania and alumina increase higher hydrocarbon selectivity. Some studies reported higher C_{2+} oxy selectivity on titania than on silica [18,47,53], but the opposite has also been reported [49,54]. Using ALD to chemically modify the silica support surface with titania and alumina, we can examine the inherent chemical effects of these three oxides without interference from those effects originating from different structural properties of the supports. In addition to studying titania and alumina as the support, we also deposit titania and alumina on calcined Rh/ SiO_2 as an overlayer, forming inverse catalyst structures. Such inverse catalysts have helped facilitate a fundamental understanding of the role of metal oxides [55–58]. However, inverse catalyst structures have mainly been prepared on model catalysts comprised of single crystals or planar films [56,59,60]. Achieving inverse catalyst structures on high surface area, powdered catalysts, which is done in the present study, could improve the understanding of the roles played by oxide overlayers under practical reaction conditions.

The dispersion of Rh nanoparticles, CO adsorption properties, and syngas conversion activity and selectivities are compared among Rh catalysts supported on original and ALD-modified silica, as well as for inverse catalysts with titania and alumina overlayers. Compared to Rh supported on silica, titania as both a support layer and overlayer is found to increase the overall activity and the selectivity toward higher hydrocarbons. On the other hand, whereas an alumina support layer led to smaller Rh nanoparticle size and increased activity, an alumina overlayer reduced syngas conversion activity. Other changes in selectivity were minor, with a slight increase in methanol selectivity observed with the addition

of alumina and no improvement in C_{2+} oxy selectivity achieved with either titania or alumina.

2. Methods

2.1. Catalyst synthesis

SiO_2 (Davisil grade 643, Sigma-Aldrich) was used as the basic support material to prepare all Rh catalysts studied in this work. Before Rh deposition or any ALD processes, the silica gel was washed in 2 M nitric acid under 80 °C for 2 h to remove iron and sodium impurities [22], then washed in deionized water to remove residual nitric acid, and finally dried at 120 °C for 24 h. Rh was deposited by incipient wetness impregnation (IWI) onto SiO_2 , or onto SiO_2 modified by ALD titania or alumina layers. For IWI synthesis, an appropriate amount of rhodium (III) nitrate hydrate (Sigma-Aldrich, 36 wt% Rh) was dissolved in Milli-Q water to achieve Rh loading of 1 wt%, and the solution volume equaled the pore volume of the silica. This solution was added onto the silica gel in a dropwise fashion, followed by drying at room temperature for 24 h and calcination in static air at 350 °C for 4 h.

2.2. ALD deposition of Al_2O_3 and TiO_2

ALD of Al_2O_3 and TiO_2 was performed in a GemStar 6 reactor (Arradiance Inc.). Al_2O_3 was deposited using trimethylaluminum (TMA, Aldrich, 97%) and deionized water as precursors (both at room temperature) at a reactor temperature of 125 °C, and TiO_2 ALD was performed at 200 °C using titanium isopropoxide (TTIP, Aldrich, 97%) and deionized water as precursors. TTIP was maintained at 65 °C. The standard ALD procedure on Si wafers is conducted under 40 sccm N_2 flow (base pressure 583 mTorr) and the pulse time and pressure increase for each precursor and H_2O are: TMA 30 ms, 8 mTorr; H_2O 30 ms, 20 mTorr for Al_2O_3 deposition; TTIP 100 ms, 8 mTorr; H_2O 1000 ms, 110 mTorr for TiO_2 deposition. For ALD deposition on silica gel, the pulse and purge times were increased and a “soaking period”, during which the deposition chamber was isolated from the pump, was applied to allow sufficient time for mass transport and adsorption of the precursor into the high surface area support. Al_2O_3 was deposited on silica gel with a pulse time of 100 ms for both precursors followed by a 30 s soaking period after each precursor dose. After soaking, the chamber was redirected to the vacuum pump and a 40 sccm N_2 purge of 180 s was applied. TiO_2 ALD was performed on silica gel with 400 ms TTIP and 4500 ms H_2O pulses. The soaking period and purge time were 30 s and 180 s, respectively, after each precursor pulse. The growth per cycle of Al_2O_3 and TiO_2 measured by ellipsometry on a planar Si wafer is 1.1 Å/cycle and 0.3 Å/cycle, respectively. Five cycles of Al_2O_3 ALD and seven cycles of TiO_2 ALD were deposited as support modification layers. The same number of cycles was also applied to form the Al_2O_3 and TiO_2 overlayer structures on SiO_2 -supported Rh catalysts.

We use the following notation to describe the different catalyst structures: the silica supports modified by Al_2O_3 and TiO_2 ALD are designated as $\text{Al}_2\text{O}_3/\text{SiO}_2$ and $\text{TiO}_2/\text{SiO}_2$; Rh supported on SiO_2 and ALD-modified SiO_2 are designated as Rh/ SiO_2 , Rh/ $\text{TiO}_2/\text{SiO}_2$, and Rh/ $\text{Al}_2\text{O}_3/\text{SiO}_2$, while the Rh catalysts with ALD overlayers are designated as $\text{Al}_2\text{O}_3/\text{Rh}/\text{SiO}_2$ and $\text{TiO}_2/\text{Rh}/\text{SiO}_2$.

2.3. Catalyst characterization

To determine the catalyst surface area, Brunauer-Emmett-Teller (BET) analysis was performed by N_2 physisorption at –196 °C using a Quantachrome Autosorb iQ3 system. Pore size distribution and pore volume were determined using the desorption isotherm,

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