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Catalyst stabilization by stoichiometrically limited layer-by-layer overcoating in liquid media

Florent Héroguel[1], Benjamin P. Le Monnier[1], Kristopher S. Brown, Juno C. Siu, Jeremy S. Luterbacher*

Laboratory of Sustainable and Catalytic Processing, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

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ABSTRACT

The use of metal oxide overcoats over supported nanoparticle catalysts has recently led to impressive improvements in catalyst stability and selectivity. The deposition of alumina is especially important for renewable catalysis due to its robustness in liquid-phase conditions. However, there are limited reports of work on alumina deposition and stabilization that goes beyond atomic layer deposition (ALD). Here, we present a layer-by-layer deposition technique for the controlled formation of conformal alumina overcoats in the liquid phase. This technique is easy to perform in common wet chemistry conditions. Alternated exposure of the substrate to stoichiometric amounts of aluminum alkoxide and water in liquid-phase conditions leads to the formation of a porous overcoat that was easily tunable by varying synthesis parameters. The deposition of 60 Al_2O_3 layers onto Al_2O_3-supported copper nanoparticles suppressed irreversible deactivation during the liquid-phase hydrogenation of furfural – a key biomass-derived platform molecule. The porous overcoat leads to highly accessible metal sites, which significantly reduces the partial site blocking observed in equivalent overcoats formed by ALD. We suggest that the ease of scalability and the high degree of control over the overcoat's properties during liquid-phase synthesis could facilitate the development of new catalyst overcoating applications.

1. Introduction

Stability has a huge influence on the industrial viability of catalytic materials. Catalyst deactivation incurs significant costs due to the need for material regeneration and eventual replacement, and therefore has been a major focus in petrochemical research [1]. Reversible deactivation is often due to coverage of the active site by chemical binding (e.g. poisoning) or coverage of the active site (e.g. coking) [1,2]. These forms of chemical deactivation can often be reversed by thermal treatment such as calcination with air. Irreversible deactivation is much more costly and is often due to physical or thermal processes [2,3]. Prominent irreversible deactivation mechanisms include support collapse, and coalescence or leaching of metal nanoparticles. Coalescence refers to the loss of active surface by metal nanoparticle aggregation through Ostwald ripening or sintering. Leaching refers to metal dissolution and occurs principally in solution.

Because most fossil-derived molecules are volatile, refineries largely rely on gas phase catalysis. The shift to renewable substrates often involves liquid-phase catalytic processing. Such conditions are required because biomass-derived molecules usually have low volatility and are produced by biomass depolymerization or biological transformation in dilute aqueous or solvent streams [4–6]. Irreversible deactivation, including by sintering and leaching, tends to be more pronounced in liquid-phase conditions, which makes catalyst stability even more critical [1,2,7].

Catalyst overcoating by deposition of a metal oxide layer is a promising method to curtail irreversible deactivation. Several overcoating methods have been shown to protect metal nanoparticles against thermal deactivation, and in some cases, coking. These methods include the use of atomic layer deposition (ALD) of alumina [8–10] and silica deposition by sol-gel [11–13]. Atomic layer deposition of alumina involves the subsequent exposure of the substrate to reactive alumina precursors or water in near-vacuum conditions. Each cycle leads to the deposition of an atomically thick layer of alumina, which allows very accurate control of the overcoat's thickness. However, the near-vacuum conditions lead to high set-up costs and limit scale-up possibilities. Furthermore, ALD conditions lead to the formation of a dense overcoat, which completely blocks access to the metal. Catalytic activity is only recovered after

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* Corresponding author.
E-mail address: jeremy.luterbacher@epfl.ch (J.S. Luterbacher).

[1] These authors contributed equally.

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a calcination step that crystallizes and cracks the overcoat [10]. However, even after calcination, access to the metal is typically significantly reduced. In comparison, overcoating with SiO_2 by sol-gel chemistry is low-cost and easy to scale up. Although the degree of control does not match ALD's, the overcoat's thickness can be kinetically controlled within a few nm due to the low reactivity of siloxide precursors [14,15]. The utility of silica overcoating is nevertheless limited by silica's low stability in high temperature liquid-phase conditions, which lead to rapid structural collapse [16].

Alumina is much more resistant in liquid-phase conditions, but the reactivity of its alkoxy precursors make its deposition difficult to control kinetically. Because of this, there are few practical liquid-phase synthesis methods for producing alumina overcoats. Instead, attempts to deposit alumina using sol-gel techniques have focused on mimicking the layer-by-layer approach and purge sequences of ALD. Such methods have been reported for several oxides including titania [17–19], alumina [20,21] and zirconia [21] and involve the subsequent exposure of the catalyst to metal precursor and aqueous solutions. Multiple washes are performed between exposures to avoid precipitation of material off the surface. The powder is then dried and calcined to obtain a single molecular layer of oxide. These steps are repeated multiple times to achieve a conformal overcoat. This method is precise but extremely time-consuming, and its multiple steps make it as difficult to scale-up as ALD. Furthermore, calcination between each deposition step prevents tuning of the overcoat.

Here, we present a simple method for the liquid-phase deposition of conformal alumina overcoats. Our technique is based on the alternated exposure of the substrate's hydroxyl groups to metal oxide precursors and water. Instead of purging excess precursor, we subsequently inject stoichiometric amounts of reactants to avoid side-reactions with unreacted excess precursor. This method enables fast and straightforward cycling and overcoat deposition. We demonstrate that, like ALD, our overcoat stabilizes a supported Cu/Al_2O_3 catalyst during the liquid-phase hydrogenation of biomass-derived furfural. This stabilization occurs despite the fact that the overcoat is significantly more porous than that obtained with ALD, thus retaining high copper accessibility.

2. Experimental

2.1. Chemicals and materials

All commercial chemicals were analytical reagents, and were used without further purification unless otherwise noted. Copper nitrate trihydrate (99.999-Cu%) was purchased from ABCR. The concentrated hydrochloric acid aqueous solution (*ca.* 37%) was purchased from Merck. The concentrated nitric acid aqueous solution (*ca.* 68%) was obtained from Sigma-Aldrich. Synthetic air (99.999%), hydrogen (99.999%), helium (99.9999%), N_2O (99.99%)/helium (99.999%) 1/99 vol./vol. and nitrogen (99.999%) were obtained from Carbagas. Silicon carbide (100 mesh) was purchased from Strem. Furfural (99%) was purchased from Acros organic, purified by distillation under reduced pressure and stored under inert atmosphere. Aluminum sec-butoxide (97%) was purchased from Merck, purified by distillation under reduced pressure and stored over 4 Å molecular sieves (Merck) under inert atmosphere. Alumina (37 m^2/g, Nano Arc) was purchased from Alpha Aesar and calcined for 12 h at 500 °C (5 °C/min) under a flow of air (100 mL/min). 1-butanol (99.5%) was purchased from Acros. 2-butanol (99%) was purchased from Sigma-Aldrich, dried over magnesium, distilled, stored over 4 Å molecular sieves (Merck) and degassed under vacuum. Water was purified using a Millipore Milli-Q Advantage A10 water purification system to a resistivity higher than 18 MΩ.cm.

2.2. Catalyst preparation

2.2.1. Preparation of alumina-supported copper NPs by incipient wetness impregnation

The alumina support was pretreated under vacuum ($< 10^{-3}$ mbar) at 150 °C (heated to temperature with a 5 °C/min ramp) for 12 h and stored in a nitrogen filled glovebox prior to impregnation. A suitable amount of copper nitrate trihydrate was dissolved in a 0.1 M nitric acid aqueous solution and added dropwise to the support until incipient wetness was reached. The resulting powder was dried for 12 h at 95 °C in air, reduced for 5 h under H_2 flow (300 °C, heated to temperature with a 1 °C/min ramp) and finally passivated at room temperature with air pulses carried by a flow of N_2.

2.2.2. Deposition of porous alumina overcoat

The catalysts were pretreated under vacuum ($<10^{-3}$ mbar) at 300 °C for 5 h and kept under inert atmosphere using Schlenk techniques and a nitrogen-filled glovebox (typically <0.5 ppm H_2O and <0.5 ppm O_2). The powder was dispersed by magnetic stirring in anhydrous 2-butanol and the mixture was heated to 60 °C. A solution was prepared for each precursor in a Schlenk flask by dissolving the appropriate amounts of water and aluminum sec-butoxide, respectively, in 2-butanol. 0.5 mL of the precursor solution (corresponding to coverage by a single monolayer) were alternatively injected every 15 min using syringes. The coverage of a single monolayer was estimated by a volume projection of the precursor molecule. This projected area was estimated using the MarvinSketch ChemAxon software. The quantity of material needed for a single layer per catalyst surface was calculated from this calculated area for a single complex.

Typically, cycles were repeated 15, 30, 45 or 60 times to obtain different overcoat thicknesses. The overcoated catalyst was separated by centrifugation (4000 rpm, 5 min), washed twice with 2-butanol (40 mL) and twice with water (40 mL). Finally, the collected powder was dried in an oven for 12 h at 150 °C (heated to temperature with a 2 °C/min ramp).

2.3. Catalytic testing

Furfural hydrogenation was investigated using a packed bed down flow tubular reactor (i.d = 4.5 mm). Typically, 0.2 g of catalyst were diluted into a bed of silicon carbide within the heated zone of the reactor, which was delimited by conductive aluminum blocks placed within the oven. The reactor was leak-tested under 30 bar of nitrogen pressure.

Before the first run, the catalyst was pretreated under air flow (100 mL/min) for 1 h at 300 °C (heated to temperature with a 2 °C/min ramp), cooled down to 30 °C under nitrogen flow (100 mL/min) and reduced under H_2 flow (100 mL/min) for 5 h at 300 °C (heated to temperature with a 1 °C/min ramp). After cooling down to the reaction temperature (130 °C), hydrogen flow was set to 35 mL/min using a Brooks mass flow controller and pressure was adjusted to 23 bar using a Tescom back pressure regulator. A furfural solution (70 g/kg in 1-butanol) was then pumped through the reactor using SSI Series II HPLC pump at 0.10 mL/min. Liquid samples were collected using a gas-liquid separator. Gas phase analyses were performed on an Agilent Technologies 7890 A gas chromatography apparatus equipped with a flame ionization detector (FID) and a HP-5 column (50 m, 0.32 mm).

After reaction, furfural flow was stopped and the catalyst was regenerated by calcination under a flow of air (400 °C, 1 h, heated to temperature with a 2 °C/min ramp, 100 mL/min) and reduction under hydrogen flow (300 °C, 5 h, heated to temperature with a 1 °C/min ramp, 100 mL/min).