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# Controlled deposition of titanium oxide overcoats by non-hydrolytic sol gel for improved catalyst selectivity and stability

Florent Héroguel [1], Luca Silvioli [1], Yuan-Peng Du, 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

Advances in the synthetic control of surface nanostructures could improve the activity, selectivity and stability of heterogeneous catalysts. Here, we present a technique for the controlled deposition of $TiO_2$ overcoats based on non-hydrolytic sol-gel chemistry. Continuous injection of $Ti(^iPrO)_4$ and $TiCl_4$ mixtures led to the formation of conformal $TiO_2$ overcoats with a growth rate of 0.4 nm/injected monolayer on several materials including high surface area SBA-15. Deposition of $TiO_2$ on SBA-15 generated medium-strength Lewis acid sites, which catalyzed 1-phenylethanol dehydration at high selectivities and decreased deactivation rates compared to typically used HZSM-5. When supported metal nanoparticles were similarly overcoated, the intimate contact between the metal and acid sites at the support-overcoat interface significantly increased propylcyclohexane selectivity during the deoxygenation of lignin-derived propyl guaiacol (89% at 90% conversion compared to 30% for the uncoated catalyst). For both materials, the surface reactivity could be tuned with the overcoat thickness.

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## 1. Introduction

Metal oxides with uniform composition are omnipresent in catalysts and catalyst supports due to their ease of production, but their use can lead to low selectivity and stability due to the lack of precise design of their surface functionalities. Deposition of thin metal oxide layers on the surface offers the opportunity to create optimal environment on the material surface [1–6]. Multiple studies demonstrate that liquid phase sol-gel based techniques can be used for the controlled growth of oxide films [7–11]. The mild operative conditions and relatively simple equipment needed for sol-gel applications make these synthetic routes appealing, especially as scale-up is considered. However, while high levels of control have been reported for $SiO_2$ deposition, which benefits from kinetically slow hydrolysis/condensation [13], highly reactive titanium oxide precursors prevent controlled deposition of thin oxide layers (<50 nm). Although remarkable results were achieved by controlling the kinetics of condensation with catalysis [14] or chelating agents [15], deposition of multiple oxide layers on challenging substrates such as high surface area mesoporous materials or supported metal nanoparticles remains a challenge [16–20].

The most versatile and powerful techniques for thin film deposition on high surface area catalyst powders such as Atomic Layer Deposition (ALD) rely at present on complex instrumentation and gas phase operations. ALD [21] is the most prominent of these techniques and has been employed to improve selectivity [22] and stabilize supported nanoparticles against sintering [2,3,23]. However, ALD requires cumbersome instrumentation and is difficult to scale up, especially on high surface area materials and powders. In addition, gas phase synthesis offers limited possibilities for tuning material porosity and structure compared to liquid phase synthesis. Tilley and coworkers developed a thermolytic molecular approach, which allowed the generation of multicomponent oxides such as Ti-Si [24] as well as various surface modifications [25], but deposition was limited to one molecular layer [26]. In addition to overcoating strategies, high-temperature calcination and reduction were also employed to cover Co particles with a titanium oxide layer, leading to improvements in catalyst stability and changes in selectivity thanks to strong metal-support interaction during aqueous-phase hydrogenation of furfuryl alcohol [27].

Non-hydrolytic sol-gel (NHSG) chemistry is a well-known technique for material synthesis and has been previously used for catalyst synthesis [28,29]. However, we have found limited

* Corresponding author.
*E-mail address:* jeremy.luterbacher@epfl.ch (J.S. Luterbacher).
[1] These authors contributed equally and are listed alphabetically.

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use of sol-gel chemistry for the deposition of thin oxide films and its effect on catalysis. NHSG precursors were used for the layer-by-layer deposition of $TiO_2$ on SBA-15 [30]. However, the alternated manual precursor addition for each half layer limited the control on the overcoat deposition and no effects on catalytic properties were reported. Similarly, ALD was used to deposit $TiO_2$ films over $Co/TiO_2$ catalysts to prevent sintering and leaching of cobalt nanoparticles [31]. However, no selectivity or reactivity effects were demonstrated beyond reduced deactivation.

In this study, we introduce a new titanium oxide thin film deposition methodology based on non-hydrolytic sol-gel (NHSG) chemistry. Our deposition is carried out in a single liquid phase step involving the continuous injection of a mixture of NHSG precursors and results in uniform coatings that are comparable in conformality to those obtained with ALD, even for high surface area materials. More importantly, we demonstrate that the selectivity of both a high-surface area homogeneous oxide catalyst (SBA-15) and a supported metal catalyst ($Pt/SiO_2$) can be significantly enhanced and controlled with the thickness of the overcoat for several reactions.

## 2. Materials and methods

### 2.1. Chemicals and materials

All reagents and solvents were analytical grade, obtained from commercial suppliers and used without further purification, unless otherwise noted. Air and moisture-sensitive reagents were handled using a nitrogen filled glove box and Schlenk techniques. Titanium isopropoxide (98%) was obtained from Acros and distilled under reduced pressure. Titanium tetrachloride (99%), tetramethyl orthosilicate (TMOS, 99%), Pluronic 123 (P123, average $M_n$ ~5800), styrene (≥99.5%), 3-propylguaiacol, isooctane (99%), tetraethylorthosilicate and 1-phenylethanol (98%) were obtained from Sigma-Aldrich. Ethanol (99%) was obtained from Fisher Scientific. 1,4-dioxane (99.8%) was obtained from ABCR. Hydrogen hexachloroplatinate(IV) hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, 99.9%) was obtained from Strem. Aerosil $TiO_2$ P25 was obtained from Evonik. $TiO_2$ PC500 was provided by Crystal. Siral40 was provided by Sasol. Toluene (VWR, 99.5%) and diethyl ether (99%, Fisher Scientific) were dried over sodium-benzophenone (99%, Sigma-Aldrich), distilled and stored over 4 Å molecular sieves (Merck) under a nitrogen atmosphere. Aqueous solutions of ammonia ($NH_4OH$ ca. 25 wt.%, ACS reagents) and hydrochloric acid (HCl ca. 37 wt.%, ACS reagents) were diluted with water purified using a Millipore Milli-Q Advantage A10 water purification system to a resistivity higher than 18 MΩ·cm. Synthetic air (99.999%), hydrogen (99.999%), helium (99.9999%) and nitrogen (99.999%) were obtained from Carbagas. The zeolite HZSM-5 was obtained by calcination of $NH_4$ZSM-5 (ABCR, 23:1 mole ratio) at 550 °C (10 °C/min ramp) for 12 h under air flow (100 mL/min). Silica spheres were prepared according to the Stöber process [32].

### 2.2. Materials synthesis

#### 2.2.1. Cuprous oxide nanoparticles synthesis

$Cu_2O$ nanoparticles were prepared by mixing aqueous solutions 1 M of $CuSO_4{\cdot}5H_2O$ with 1 M of reducing agent $Na_2S_2O_3$ in volumetric proportion of 1:4. The mixture was then poured into an Erlenmeyer flask containing equivolumetric amount of 1 M sodium hydroxide. A bright orange precipitate appeared almost instantaneously, indicating that the copper was precipitating under the form of cuprous oxide. The solution was vigorously stirred for 30 min. The mixture was centrifuged and the collected particles washed four times with water and once with ethanol. The sample was then dried overnight under vacuum at 65 °C.

The materials were annealed at 200 °C (1.5 °C/min ramp) for 2 h under inert gas ($N_2$) flow to increase their stability toward air oxidation. This synthetic route reportedly yields (1 1 1) plane-oriented cuprous oxide nanoparticles [33].

#### 2.2.2. Supported platinum nanoparticle synthesis

$Pt/SiO_2$ and $Pt/TiO_2$ were prepared by incipient wetness impregnation of the support with a 0.1 M HCl aqueous solution of $H_2PtCl_6{\cdot}6H_2O$, calcination at 500 °C in a muffle furnace and reduction under $H_2$ flow (100 mL/min) at 300 °C (2 °C/min ramp) for 10 h.

#### 2.2.3. SBA-15 synthesis

The synthesis of mesoporous silica SBA-15 was based on methods found in literature [34–37]. Pluronic 123 (7.0 g) was dissolved in a 1.6 M aqueous HCl solution (262.5 g) in a round bottom flask and heated to 35 °C in oil bath. Then, TMOS (10 mL) was added to start the synthesis, stirring the solution vigorously for 1 min followed by moderate stirring for 24 h. Afterward, a hydrothermal treatment under static conditions at 140 °C was performed for an additional 24 h. This was followed by filtration, and a day-long Soxhlet extraction with ethanol. The sample was then dried in a ventilated oven at 90 °C for 12 h. Finally, the acquired solid was calcined in a muffle furnace for 6 h at 500 °C (1 °C/min ramp).

#### 2.2.4. Overcoating representative procedure

The substrate (0.5 g) was loaded into a double neck round bottom flask and dried for 12 h at 150 °C under vacuum ($<10^{-2}$ mbar). After refilling the flask with nitrogen, the solid was suspended in anhydrous toluene (20 mL) and sonicated for 10 min to ensure uniform particle dispersion. A reflux condenser was fitted to the flask and the suspension was stirred at 110 °C. The precursor solution was prepared under inert atmosphere by dissolving appropriate amounts of $TiCl_4$ and freshly distilled $Ti(O^iPr)_4$ in anhydrous toluene to yield a molar ratio $[Ti]/[^iPrO] = 1$. Concentrations were adjusted to achieve one monolayer per mL, calculated from the ratio of the titania precursor's projected surface area (determined from its Van der Waals volume projection as described in our previous work [38]) and the substrate surface area. The precursor solution was added to the refluxing suspension through a rubber septum using a gas-tight glass syringe (Hamilton, US) with a PTFE plunger and an automatic syringe pump (KDS 100 legacy). The needle was kept at a distance of at least 10 cm from the mixture to avoid premature $TiO_2$ condensation on the needle tip (Fig. S2). The addition rate was typically set to one monolayer per hour, or 0.5 monolayer per hour for high surface area substrates (>100 $m^2/g$). After completing the precursor addition, the mixture was stirred for 2 h and cooled to 80 °C. Then, 20 mL of anhydrous diethyl ether were added to quench unreacted Ti—Cl bonds and the mixture was stirred for another 12 h. The solid was collected by centrifugation (5 min, 4500 rpm) and washed three times with 50 mL diethyl ether, twice with 50 mL ethanol, before being redispersed in $H_2O$. Aging of the as-synthesized overcoat was performed by stirring the material for 12 h at 70 °C in an aqueous solution of 0.2 M $NH_4OH$. Finally, the solid was isolated by filtration, dried under vacuum at 80 °C and calcined for 5 h at 500 °C (2 °C/min ramp) under flow of synthetic air.

### 2.3. Material characterization

#### 2.3.1. Inductively coupled plasma optical emission spectrometry (ICP-OES)

Elemental analyses were performed at the EPFL Central Environmental Laboratory using inductively coupled plasma optical emission spectrometry (ICP-OES) on an ICPE-9000 Multitype

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