



Priority Communication

Titania-supported gold-based nanoparticles efficiently catalyze the hydrodeoxygenation of guaiacol



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ABSTRACT

Well-defined Au, Rh and AuRh nanoparticles were synthesized by colloidal chemical co-reduction, immobilized on rutile titania nanorods, and evaluated in the gas-phase hydrodeoxygenation (HDO) of guaiacol, an important product of lignin pyrolysis. Au/TiO₂ appears active, stable and selective for the HDO of guaiacol to phenol in broad temperature and conversion ranges, making this model catalyst the first reported example of gold efficiency for the hydroprocessing of a lignin derivative. Furthermore, upon nanoalloying Au with Rh, the main HDO product at 280 °C switches from phenol to cyclohexane, which is tentatively ascribed to a cooperative effect.

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1. Introduction

Catalytic hydrodeoxygenation (HDO) is one of the most viable processes for converting lignocellulosic biomass into fuels and chemicals. Guaiacol (2-methoxyphenol) is typically present in bio-oils obtained from lignin pyrolysis, and is refractory to the deoxygenation process [1–3]. The drawbacks of conventional HDO catalysts, Co- or Ni-promoted Mo sulfides, which have been widely applied to HDS(hydrodesulfurization)-HDO co-processing [4,5], are the possible contamination of products by incorporation of sulfur, or the catalyst deactivation in the absence of sulfiding agent in the feed [1,6,7]. Beyond sulfides, transition-metal nitrides and phosphides have also been successfully tested in guaiacol HDO [8,9]. However, supported Pt-group metals have been found the most active, and can therefore be used at lower temperatures and/or pressures [10]. Studies of zirconia-supported noble metal catalysts for guaiacol HDO have shown the superior activity and stability of Rh over the other noble metals and the sulfides [11,12]. In addition, several works have suggested the potential interest of noble metal-based bimetallic catalysts for biomass valorization [2,3,13]. The nature (an acidity) of the support has a major influence on the mechanism of HDO, and supports such as carbon or titania decrease the sensitivity to water vapor observed for conventional alumina [7,14–16]. Acidic supports have been

reported to enhance the catalytic activity for deoxygenation. The bifunctional catalysts should possess an optimal combination of the hydrogenation function of a noble metal with the deoxygenation ability of support acid sites [17]. Furthermore, a recent study of guaiacol HDO on Ru/TiO₂ has demonstrated the efficiency of the rutile phase as support for stabilizing the metal particles [15]. To our knowledge, neither Rh/TiO₂ nor any gold-based catalyst has ever been investigated for the hydroprocessing of a lignin derivative.

In this work, we have used Au/TiO₂, Rh/TiO₂ and AuRh/TiO₂ catalysts prepared by the same colloidal co-reduction method, to perform the HDO of guaiacol in a continuous flow reactor under hydrogen pressure. We report that the three catalysts show good performances in this reaction, although with very different selectivities. Au/TiO₂ catalyzes guaiacol HDO with a high selectivity to phenol, while Rh/TiO₂ leads to a broader range of deoxygenated and mono-oxygenated products and bimetallic AuRh/TiO₂ exhibits a high selectivity to O-free products. These distinct behaviors are discussed in light of the catalyst structural properties.

2. Experimental

2.1. Catalyst preparation

TiO₂ rutile nanorods were prepared using a simplified procedure based on a hydrothermal method reported by Li and Afanasiev [18]. 10 g of commercial Degussa P25 TiO₂ (50 m²/g) and

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100 mL of 15 wt% H₂SO₄ solution were mixed in a Teflon reactor and placed in a sealed autoclave kept at 200 °C for 15 days. The obtained solid was washed several times with 0.1 M NH₄NO₃ to remove adsorbed sulfate, then washed with distilled water, dried at 100 °C overnight, and calcined at 350 °C in air for 2 h. AuRh NPs, along with their monometallic counterparts, were prepared by a colloidal chemical (co)reduction route [19] adapted from Toshima, Prati, Hutchings, and coworkers [20–24]. The metal precursors were HAuCl₄·3H₂O (Strem Chemicals, 99.9%, 49 wt% Au) and RhCl₃·nH₂O (Sigma-Aldrich, 99.9%, 38–40 wt% Rh). In a first step, a 200 mL aqueous solution containing the two metallic precursors was prepared by adding the amounts of precursors necessary for reaching an Au loading of 2 wt% and/or a Rh loading of 1 wt%. Next, a 1 wt% aqueous solution of a stabilizing agent, polyvinyl alcohol (PVA, Mw = 10,000) was added to the preceding solution while keeping always a mass ratio $m_{\text{PVA}}/m_{\text{metal}}$ of 1.2. A solution of 0.1 M NaBH₄, freshly prepared and kept at 0 °C before use, was then dropped under stirring into the metallic precursor solution with a molar ratio $n_{\text{NaBH}_4}/n_{\text{metal}}$ of 5. Stirring was then maintained for 30 min to allow the complete decomposition of the remaining NaBH₄ excess. The solution was then acidified to pH 3.5 by addition of 0.01 M HCl in order to favor the sol immobilization onto the TiO₂ support. The amount of support necessary for reaching the final metal loading was then added and stirring was continued for 3 h. Finally, the material was filtered, washed several times with hot distilled water (70 °C), and dried in air at 100 °C overnight.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) analyses were performed with an aberration-corrected FEI ETEM Titan G2 (CLYM) operated at 300 kV and a Jeol JEM 2010 operated at 200 kV. The samples were crushed in ethanol and the solution was ultrasonically stirred before dropping on a holey carbon-covered copper TEM grid, followed by drying.

The metal concentrations were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES, Activa instrument from Horiba Jobin Yvon). In order to dissolve them completely, the samples were treated with a mixture of H₂SO₄, aqua regia and HF at 250–300 °C.

2.3. Catalytic testing

The guaiacol HDO reaction was performed in a gas-phase continuous flow reactor under H₂ pressure (4 MPa) between 240 and 300 °C. Before the catalytic tests, the as-prepared catalysts were reduced in the reactor under pure hydrogen flow (60 NmL/min) at 300 °C for 1 h. The whole catalytic bench has been previously described elsewhere [6]. The solid catalyst was placed on a frit located in a tubular glass tube, which was itself inserted into a tubular stainless-steel reactor. A 2.7 kPa partial pressure of guaiacol was generated by flowing H₂ (60 NmL/min) in a saturator (130 °C)/condenser (116 °C) system containing liquid guaiacol (Acros Organics, 99% purity). The tested catalyst weight comprised between 50 and 100 mg, corresponding to weight hourly space velocities (WHSV) between 6 and 3 h⁻¹, respectively. The gas flows and the total pressure were controlled using mass-flow controllers and a back-pressure regulator, respectively. The products were analyzed online using a gas chromatograph (HP 5890 II) equipped with a flame ionization detector and a Varian CPSIL-5 column (50 m × 0.32 mm × 5 μm). The condensed products (LN₂ trap) were also analyzed by gas chromatography coupled with mass spectrometry (GC-MS Agilent 5975B). The product identification was confirmed by manual injection of pure compounds. Response factors were determined theoretically and experimentally depend-

ing on the products, and used for checking the molar balance and measuring the selectivities. Methane and methanol, which were inherently formed during HDO reactions and detected online by GC, together with water, are not accounted for in the selectivity data in order to focus on the (most interesting) C₆-C₈ products. However, taking their presence into account, the molar balance was close to 98% for all experiments.

3. Results

3.1. Catalyst preparation and characterization

Au, Rh, and AuRh nanoparticles were synthesized by conventional colloidal chemical co-reduction in water, using chloride salts as metal precursors, polyvinyl alcohol (PVA) as a surfactant, and NaBH₄ as a reducing agent. Then, a powder of single-phase rutile titania nanorods synthesized using a hydrothermal method was added to the acidified colloidal suspension, which led to the immobilization of PVA-embedded nanoparticles on the titania support (Section 2.1) [19]. The metal loadings of the resulting catalysts are 1.75 wt% Au, 0.62 wt% Rh and 1.58 wt% Au + 0.68 wt% Rh (*i.e.* Au₅₅Rh₄₅ molar composition), as determined by ICP-OES. Fig. 1 shows TEM images of the as-prepared TiO₂-supported Au, Rh and AuRh catalysts. In all cases, the nanoparticles are well distributed on their support and exhibit a roundish shape with a relatively sharp size distribution. The average metal particle sizes, as determined by analyzing several hundreds of nanoparticles on the TEM images, are 2.8 ± 0.8 nm, 2.4 ± 0.6 nm, and 3.3 ± 1.0 nm for Au, Rh and Au₅₅Rh₄₅, respectively. As previously reported following infrared spectroscopy and scanning TEM, after a treatment at 350 °C in H₂ flow similar to the *in situ* pretreatment performed in this work before the catalytic tests, the PVA surfactant is completely removed and the bimetallic nanoparticles adopt a Janus-type configuration with Au/Rh/TiO₂ stacking [19,25]. The observed segregation between Au and Rh is consistent with previous works on the bulk-immiscible Au-Rh system [26,27], and has been recently rationalized through DFT calculations on small clusters [25,28].

3.2. Catalyst evaluation in guaiacol HDO

Au/TiO₂, Rh/TiO₂, AuRh/TiO₂ and bare TiO₂ samples were evaluated in gas-phase guaiacol hydroconversion in a flow-fixed bed reactor under high pressure of hydrogen (4 MPa H₂, 2.7 kPa guaiacol) between 240 °C and 300 °C. Table 1 and Fig. S1 (Supporting Information) report guaiacol conversion rate data. The activities of the three noble metal-containing catalysts appear similar and much higher than those of bare TiO₂. The turnover frequencies are of 1.3–1.5 guaiacol molecules converted per surface metal atom per second at 280 °C (Table 1). As shown in the Arrhenius plot of Fig. S1, the apparent activation energy for the AuRh catalyst (112 kJ/mol) is intermediate between those for Rh/TiO₂ (88 kJ/mol) and Au/TiO₂ (126 kJ/mol).

Guaiacol HDO has been previously shown [1] to proceed mostly through demethylation, demethoxylation, hydrogenation and dehydroxylation reactions, as illustrated in Scheme 1. In a first step, guaiacol can lose a methyl group (demethylation) to form catechol, or can be demethoxylated directly to phenol. Demethylation and demethoxylation reactions proceed with the formation of methane and methanol, whose ratio depends on the catalyst and the temperature. Methylcatechol can also be formed, either from the transfer of the guaiacol methyl group (from methoxy substituent) or from catechol methylation. On metal catalysts, hydrogenation of the aromatic ring of guaiacol generally occurs, forming methoxycyclohexanol. (Methyl)catechol is dehydroxylated to

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