Catalysts for selective hydrogenation of furfural derived from the double complex salt $[Pd(NH_3)_4](ReO_4)_2$ on γ-Al_2O_3

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The double complex salt $[Pd(NH_3)_4](ReO_4)_2$ was employed as precursor of supported bimetallic catalysts for selective hydrogenation of furfural. Direct reduction of $[Pd(NH_3)_4](ReO_4)_2$ on γ-Al_2O_3 in flowing H_2 at 400 °C yields bimetallic nanoparticles 1–2 nm in size that exhibit significant interaction between the metals, as evidenced by temperature-programmed hydride decomposition (complete suppression of β-PdH_x formation), extended X-ray absorption fine structure spectroscopy at the Pd K and Re L_{III} edges (Pd—Re distance = 2.72 Å), and scanning transmission electron microscopy with energy dispersive X-ray analysis. In contrast, calcination of $[Pd(NH_3)_4](ReO_4)_2$ on γ-Al_2O_3 at 350 °C in air and subsequent reduction in H_2 at 400 °C results in metal segregation and formation of large (>50 nm) supported Pd particles; Re species cover the Pd particles and γ-Al_2O_3 support. A PdRe 1:2 catalyst prepared by sequential impregnation and calcination using $HReO_4$ and $[Pd(NH_3)_4](NO_3)_2$ has a similar morphology. The catalyst derived by direct reduction of $[Pd(NH_3)_4](ReO_4)_2$ on γ-Al_2O_3 exhibits remarkably high activity for selective hydrogenation of furfural to furfuryl alcohol (FAL) at 150 °C and 1 atm. Suppression of H_2 chemisorption via elimination of Pd threefold sites, as evidenced by CO diffuse-reflectance infrared Fourier transform spectroscopy, correlates with increased FAL selectivity.

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1. Introduction

Interest in platinum-group metal (PGM)-Re catalysts for selective hydrogenation and hydrogenolysis, specifically of biomass-derived compounds, has increased sharply in the past decade. Several groups have reported PGM-Re catalysts with enhanced activity and chemoselectivity when compared to the supported PGM alone in reactions such as glycerol reforming to synthesis gas [1,2] and selective hydrogenolysis of polyols and cyclic ethers [3–8]. The coexistence of several Re oxidation states (e.g., Re^0, Re^{4+} and Re^{7+}) in the reduced catalysts has caused uncertainty regarding the catalytically important Re species [8]. A significant difficulty in preparing supported PGM-Re bimetallic nanoparticles via conventional methods (e.g., incipient wetness impregnation) is strong interaction between Re^{7+} oxo species and metal oxide supports, particularly on γ-Al_2O_3, resulting in isolated ReO_4^- surface species [9,10] that resist reduction to the metallic state [11–13]. Most preparations of PdRe/Al_2O_3 catalysts include a calcination step, whether the catalysts are prepared by co-impregnation using a single solution containing both precursors [14] or by sequential impregnation using separate solutions [15–17]. During calcination, $[ReO_4]^-$ species wet the support surface forming up to a monolayer of Al—O—ReO_3 surface complexes [10,11,18–20]. There is also evidence that Re_2O_7 may sublime and then re-adsorb on the support contributing to the mobility of Re^{7+} species under oxidizing conditions [19,21].

Highly dispersed supported metal catalysts may contain bimetallic nanoparticles comprising metal pairs (e.g., Cu-Ru and Pt-Re) that do not form bulk solid solutions over a significant composition range [22]. Two elements that do not alloy in the bulk can become kinetically trapped in bimetallic nanostructures by large energy barriers to nucleation of a second homometallic phase [23]. Thus, although Pd and Re do not form a continuous range of bulk solid solutions [24], a suitable preparation method may nonetheless yield supported bimetallic nanoparticles. Catalyst preparation methods have been devised that promote Pd-Re interactions and minimize Re-support interactions. These include catalytic reduction, wherein chemisorbed H on the surface of Pd particles reduces perrhenate ions adsorbed from solution [25–27], and the directed deposition technique, wherein a Pd precursor is deposited on reduced Re particles [28–30]. Both of these methods, however, require preparation and handling of air-sensitive samples under an inert atmosphere, and the loading of Re (or Pd) is restricted based on the metal surface area of the parent catalyst.

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In contrast, reductive decomposition of a suitable precursor containing both metals in a fixed ratio is a comparatively simple process to facilitate the formation of supported bimetallic nanoparticles [31,32]. One such precursor, $[Pd(NH_3)_4](ReO_4)_2$, was prepared and characterized originally by Zadesenets et al. [33]. This slightly water-soluble double complex salt (DCS) consists of two perrhenate ions weakly coordinated to a square-planar tetraammine Pd^{2+} complex [34]. Reduction of the unsupported DCS has been reported to yield a Re:Pd solid solution having an *hcp* structure and 2:1 atomic ratio; however, the Pd-Re binary phase diagram indicates that a mixture of this composition should separate into Pd-rich (∼90 at.% Pd) and Re-rich (>95 at.% Re) phases [24]. We are aware of only one example of the use of this DCS in catalyst preparation: a patent for a carbon-supported PdRe catalyst used in hydrogenation of succinic anhydride [35].

In this work, PdRe/Al_2O_3 catalysts for selective hydrogenation of furfural were prepared using $[Pd(NH_3)_4](ReO_4)_2$ supported on γ-Al_2O_3. Direct reduction of the supported DCS minimizes strong interactions between perrhenate species and the γ-Al_2O_3 support and results in nearly simultaneous and complete reduction of both metals. PdH_x formation is suppressed completely in the reduced catalyst evidencing a strong Pd-Re interaction. Extended X-ray absorption fine structure (EXAFS) spectroscopy results are consistent with small bimetallic nanoparticles with Pd—Re bonding at 2.72 Å. Scanning transmission electron microscopy (STEM) with energy-dispersive X-ray (EDX) analysis reveals bimetallic nanoparticles 1–2 nm in size. Calcination of the supported DCS in air prior to reduction promotes segregation of the two metals resulting in large (>50 nm) irregularly shaped Pd particles and 1–2 nm Re particles covering the Pd particles and support. A 1:2 Pd:Re catalyst prepared by sequential impregnation and calcination using $HReO_4$ and $[Pd(NH_3)_4](NO_3)_2$ has a similar morphology. The PdRe/Al_2O_3 catalysts exhibit lower H:CO chemisorption ratios, increased linear-to-bridging ratios in CO diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS), and lower furfural decarbonylation rates relative to Pd/Al_2O_3. The 1:2 Pd:Re catalyst produced via direct reduction of the supported DCS exhibits greater specific activity and a higher furfural turnover frequency (TOF) than conventionally prepared PdRe/Al_2O_3 catalysts [36].

2. Experimental methods

2.1. Catalyst preparation

$[Pd(NH_3)_4](ReO_4)_2$ was prepared by adding 4.4376 g of a 10 wt. % aqueous solution of $[Pd(NH_3)_4](NO_3)_2$ (99% metals basis, Aldrich) to a solution of 0.7950 g NH_4ReO_4 (99 + %, Alfa Aesar) in 12 mL (18 MΩ-cm) deionized (DI) water at 25 °C. Upon mixing, a light yellow salt precipitated from solution; the precipitate was filtered, washed thoroughly with DI H_2O, and dried at 25 °C (78.2% yield). Lattice parameters obtained by X-ray crystallography of the product (Supplementary Information, Table S1) agree well with those reported in [33].

Table 1 lists the precursors, calcination conditions, and metal loadings for the catalysts. Metal loadings were determined by inductively coupled plasma-optical emission spectrometry (ICP-OES) analysis at Eastman Chemical Company in Kingsport, TN. The supported DCS catalyst was prepared by wet impregnation of a high-purity γ-Al_2O_3 support (Grace-Davison MI-209, 183 m^2/g BET surface area) with $[Pd(NH_3)_4](ReO_4)_2$ (nominal loadings of 1.5 wt.% Pd and 5 wt.% Re). Because of its low solubility, impregnation was conducted at 80 °C using an aqueous slurry (10 mL solution/g support). A rotary evaporator with a bath temperature of 80 °C was used to warm the γ-Al_2O_3 support and prevent immediate precipitation of the DCS. Water was evaporated slowly under reduced pressure. When the catalyst appeared dry, it was removed from the rotary evaporator and dried in air at 110 °C overnight. A portion of the sample was calcined at 350 °C for 1 h in 0.6 L/min zero-grade air (National Welders). This sample is denoted the calcined DCS catalyst. Preparation details for the Pd/Al_2O_3, Re/Al_2O_3 and PdRe/Al_2O_3 (PdRe seq.) catalysts are published elsewhere [36]; the latter was prepared by sequential impregnation and calcination using NH_4ReO_4 and $[Pd(NH_3)_4](NO_3)_2$ precursors.

2.2. H_2 and CO chemisorption

Volumetric chemisorption measurements were performed using a Micromeritics ASAP 2020c instrument. Reported uptakes for strongly bound H_2 and CO were determined by the difference isotherm method. Samples were reduced *in situ* at 400 °C for 1 h in flowing research-grade H_2 (National Welders), evacuated at 400 °C for 2 h, and then cooled to 100 °C for H_2 chemisorption. The H_2 analysis was repeated at 70 °C and 35 °C, in order, and the samples were evacuated at 300 °C for 1 h between each analysis. Two isotherms were measured at each temperature: an initial isotherm and a second isotherm measured after evacuation to remove weakly adsorbed species. Lastly, a CO difference isotherm analysis was performed at 35 °C.

2.3. TPR and TPHD

Temperature-programmed reduction (TPR) experiments were performed using a Micromeritics 2920 Autochem II equipped with a thermal conductivity detector (TCD). H_2 uptake was measured from −50 °C by cooling the sample in ultra-high purity (UHP) He (National Welders), and then switching to 5% H_2/Ar (Machine and Welding Supply). Both gases were purified using H_2O/O_2 traps (Oxilab). Once the TCD baseline was stable, the sample was heated at 10 °C/min to 400 °C and held for 1 h. Temperature-programmed hydride decomposition (TPHD) experiments consisted of a second ramp at 10 °C/min to 400 °C after cooling to −50 °C in 5% H_2/Ar.

2.4. EXAFS spectroscopy

X-ray absorption spectra were measured at the Advanced Photon Source at Argonne National Laboratory on beamline MR-CAT-

Table 1
Catalysts, preparation details, and metal loadings.

Catalyst	Precursor(s)	Calcination	Pd loading (wt.%)	Re loading (wt.%)
DCS	$[Pd(NH_3)_4](ReO_4)_2$	None	1.41	4.72
Calcined DCS	$[Pd(NH_3)_4](ReO_4)_2$	350 °C, 1 h	_[b]	_[b]
PdRe seq[a]	NH_4ReO_4, $[Pd(NH_3)_4](NO_3)_2$	400 °C, 3 h	1.50	4.85
3% Pd[a]	$[Pd(NH_3)_4](NO_3)_2$	350 °C, 1 h	3.00	–
1.5% Pd[a]	$[Pd(NH_3)_4](NO_3)_2$	400 °C, 3 h	1.49	–
5% Re[a]	$HReO_4$	350 °C, 1 h	–	5.47

[a] Denotes catalyst described in Ref. [36].
[b] Not tested.