



Bimetallic RhRe/C catalysts for the production of biomass-derived chemicals



Mei Chia^a, Brandon J. O'Neill^a, Ricardo Alamillo^a, Paul J. Dietrich^b, Fabio H. Ribeiro^b, Jeffrey T. Miller^c, James A. Dumesic^{a,*}

^a Department of Chemical and Biological Engineering, University of Wisconsin–Madison, 1415 Engineering Drive, Madison, WI 53706, USA

^b Department of Chemical Engineering, Purdue University, 480 Stadium Mall Drive, West Lafayette, IN 47907-2100, USA

^c Chemical Sciences and Engineering Division, Argonne National Laboratory, 9700 S. Cass Ave, Building 200, Argonne, IL 60429-4837, USA

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ABSTRACT

Pretreatment temperature affects the activity of a RhRe/C catalyst for C–O hydrogenolysis of 2-(hydroxymethyl)tetrahydropyran and for dehydration of fructose. Catalytic activities for both C–O hydrogenolysis and dehydration were observed to decrease with an increase in pretreatment temperature from 393 to 723 K, which coincides with a decrease in the number of sites quantified using NH₃ temperature-programmed desorption. Results for the characterization of RhRe/C using X-ray absorption spectroscopy (XAS) are consistent with the formation of Rh-rich particles with a shell of metallic Re islands after reduction at 393 K, which shows penetration of Re into the nanoparticle with increasing reduction temperature. No evidence of rhenium oxide was found from the Re L_{III}-edge XAS spectra after reduction at temperatures above 363 K or under aqueous *operando* conditions. The apparent acidity of RhRe/C is suggested to be generated from the activation of water molecules over Re atoms on the surface of metallic Rh–Re particles.

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1. Introduction

The role of oxophilic promoters (e.g., Re) on the catalytic activity and selectivity of reducible metals (e.g., Pt and Rh) has been an area of recent interest in the literature, particularly for selective C–O scission reactions relevant to the conversion of biomass-derived feedstock. For example, the addition of Re to Pt catalysts has been shown to cause an increase in the activity for aqueous phase reforming (APR) of glycerol, and this effect was attributed to a decrease in the binding energy of CO to Pt and an increase in the water–gas-shift activity of the catalyst [1–3]. Similarly, PtMo catalysts have been reported to be effective in the APR of glycerol [4]. Various authors have also demonstrated that the addition of Re to Ru, Pt, and Ir catalysts causes an enhancement in C–O hydrogenolysis activities of glycerol and an increase in the selectivity to 1,3-propanediol compared to the corresponding monometallic catalysts [5–8]. For instance, work by Daniel et al. [8] reported that the hydrogenolysis of glycerol over Pt/C results in the formation of ethylene glycol, 1,2-propanediol, and 1-propanol as the main products with no 1,3-propanediol detected, while

selectivities of 20–35% to 1,3-propanediol were observed over PtRe/C. Furthermore, the total glycerol hydrogenolysis activity of PtRe/C was an order of magnitude higher than Pt/C.

Besides C–O scission reactions, the addition of Re to Pt and Ru catalysts has been shown to enhance activities for the hydrogenation of carboxylic acids. For example, Manyar et al. reported that the addition of Re to Pt/TiO₂ increased the hydrogenation activity for the conversion of stearic acid to stearyl alcohol compared to Pt/TiO₂, although selectivities to stearyl alcohol over PtRe/TiO₂ were decreased to 70%, compared to 93% over Pt/TiO₂ [9]. Also, the addition of Re to a Ru/C catalyst results in higher activity and stability for the hydrogenation of levulinic acid to γ -valerolactone compared to Ru/C in the presence of sulfuric acid, and the Ru–Re catalyst displayed high activity for formic acid decomposition [10].

We recently proposed that the combination of an oxophilic promoter and an easily reducible metal result in the formation of a bifunctional catalyst possessing both acid and metal sites [11]. We demonstrated this concept using results from experimental studies and first-principle density functional theory (DFT) calculations, where the reactivity trends over the RhRe/C catalyst were consistent with a bifunctional mechanism in which selective C–O hydrogenolysis proceeds through initial acid-catalyzed ring-opening or dehydration followed by metal-catalyzed hydrogenation [11]. Temperature-programmed desorption (TPD) of NH₃

* Corresponding author. Fax: +1 (608)262 5434.

E-mail address: dumesic@engr.wisc.edu (J.A. Dumesic).

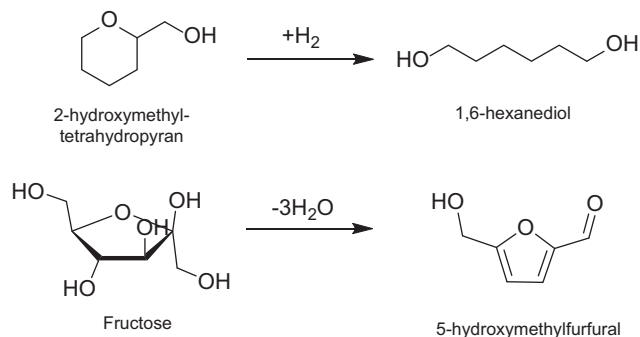


Fig. 1. Reactions discussed in this article: C–O hydrogenolysis of 2-hydroxymethyl-tetrahydropyran (HMTHP) to 1,6-hexanediol (1,6-HDO) and dehydration of fructose to 5-hydroxymethylfurfural (HMF).

was used as a means to quantify these active sites over RhRe/C, and the apparent Brønsted acidity of this catalyst was proposed to arise from the deprotonation of hydroxyl groups on rhenium atoms associated with rhodium. Similarly, recent work by Zhang et al. has reported the presence of acid sites on a PtRe/C catalyst under glycerol reforming conditions using NH₃ TPD analysis and examination of product distributions [12]; their work provides further evidence of the general bifunctional nature of this unique class of catalysts.

In the present paper, we show that the reduction temperature used to pretreat a RhRe/C (molar ratio Rh:Re = 1:0.5) catalyst prior to exposure to continuous-flow reaction conditions has a significant effect on the catalytic activity and the number of active sites quantified by NH₃ TPD. Additionally, we have studied this catalyst for an acid-catalyzed reaction that is important in biomass conversion processes: the dehydration of biomass-derived fructose to 5-hydroxymethylfurfural (HMF) (Fig. 1). [13–16] Importantly, we have studied the nature of the active sites on this RhRe/C catalyst using X-ray absorption spectroscopy (XAS) under *in situ* and *operando* conditions to probe the relationship between catalyst structure and catalytic activity.

2. Methods and materials

2.1. Catalyst preparation

Metal catalysts were prepared by incipient wetness impregnation of Vulcan XC-72 with aqueous solutions of RhCl₃ and NH₄ReO₄. The RhRe/C catalyst was obtained by successive impregnation of dried, unreduced Rh/C with NH₄ReO₄. This RhRe/C catalyst consisted of 4 wt% Rh and an atomic ratio of Rh:Re = 1:0.5. Prior to use in experiments, catalysts were dried in air (393 K), reduced in flowing H₂ (723 K), and passivated with flowing 1% O₂ in He (298 K). ZSM-5 (Engelhard, Si/Al = 30) was calcined *in situ* at 723 K for 4 h in flowing air prior to introduction of liquid feed in continuous-flow studies.

2.2. Temperature-programmed desorption

Temperature-programmed experiments were carried out using an apparatus comprised of a tube furnace connected to a variable power supply and PID temperature controller (Love Controls) with a K-type thermocouple (Omega). Reduced and passivated RhRe/C catalyst (0.3 g) was loaded into the fritted quartz tube, pretreated in flowing H₂ (100 cm³(STP) min⁻¹) at temperatures stated in the text for 4 h, and purged with He (200 cm³(STP) min⁻¹) for 90 min. NH₃ adsorption was performed at 298 K using 1% NH₃ in He, with a flow rate of 100 cm³(STP) min⁻¹. After NH₃ adsorption,

the sample was purged with flowing He (200 cm³(STP) min⁻¹) at 298 K for 90 min. The He flow rate was adjusted to 30 cm³(-STP) min⁻¹ followed by initiation of a temperature ramp at 10 K min⁻¹ from 298 to 1073 K. ZSM-5 (0.1 g) was calcined in flowing air (100 cm³(STP) min⁻¹) at 723 K for 4 h and cooled to 423 K under flowing He (100 cm³(STP) min⁻¹), followed by adsorption of NH₃ at 423 K (1% NH₃ in He, 100 cm³(STP) min⁻¹). After NH₃ adsorption, the sample was purged with flowing He (200 cm³(-STP) min⁻¹) at 423 K for 90 min and then cooled to 298 K under He flow. The He flow rate was adjusted to 60 cm³(STP) min⁻¹, followed by initiation of a temperature ramp at 10 K min⁻¹ from 298 to 1073 K. The effluent from the reactor was analyzed using an OmniStar Gas Analyzer (Pfeiffer Vacuum, Model GSD 320) using the SEM detector. The NH₃ desorption profiles reported are based on the mass 15 (NH) signal, which was verified to be directly indicative of NH₃ desorption alone and did not experience any interference from the fragmentation of contaminants such as H₂O and CO₂. The acid site density for ZSM-5 was determined to be 524 μmol g⁻¹ using NH₃ TPD analysis.

2.3. Batch reaction experiments

Reactions were carried out using a 50 mL pressure vessel (Hastelloy C-276, Model 4792, Parr Instrument). After loading the reactant solution, catalyst, and magnetic stir bar into the reactor, the vessel was sealed, purged with 34 bar He, and pressurized with 34 bar H₂. Mechanical stirring was maintained using a magnetic stirrer plate (500 rpm).

2.4. Continuous-flow reaction experiments

The flow reactor was a 6.4 mm (0.25 in.) outer diameter stainless steel tube with wall thickness of 0.7 mm (0.028 in.). The reactor was heated with a furnace composed of close-fitting aluminum blocks externally heated by an insulated furnace (1450 W/115 V, Applied Test Systems Series 3210), and temperature was monitored using a K-type thermocouple (Omega) placed outside the reactor. Temperature was controlled with a PID temperature controller (Love Controls, Series 16A). Liquid feed solution was introduced into the reactor with co-feeding of gas (i.e., He (fructose dehydration reactions) or H₂ (2-(hydroxymethyl)tetrahydropyran (HMTHP) C–O hydrogenolysis reactions)) in an up-flow configuration. A high-performance liquid chromatography (HPLC) pump (LabAlliance, Series 1) was used to control the liquid feed rate. Gas flow was controlled with a mass-flow controller (Brooks 5850 model), and the system pressure was maintained by passing the effluent gas stream through a back-pressure regulator (GO Regulator, Model BP-60). The effluent liquid was collected in a gas-liquid separator and drained periodically for analysis by HPLC. The system was determined to be free of mass transfer limitations by the Weisz–Prater criterion [17].

2.5. Analytical methods

Quantitative analyses were performed using a Waters 2695 separations module HPLC instrument equipped with a differential refractometer (Waters 410), a photodiode array detector (Waters 996), and an Aminex HPX-87P column (Biorad) at 358 K, with Milli-Q water at a flow rate of 0.6 mL min⁻¹ as the mobile phase. The possible presence of rhenium in solution was investigated using inductively coupled plasma atomic emission spectrometry (ICP-AES).

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