



Effects of support identity and metal dispersion in supported ruthenium hydrodeoxygenation catalysts



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ARTICLE INFO

Article history:

Received 16 December 2013

Received in revised form 11 February 2014

Accepted 19 February 2014

Available online 28 February 2014

Keywords:

Hydrodeoxygenation

Ru heterogeneous catalyst

Formate Assisted pyrolysis oils (FAsP)

EXAFS

Biofuels

TiO₂

MCM-41

SBA-15

ABSTRACT

Substituted phenols are the most recalcitrant oxygenates in conventional pyrolysis oils and the dominant oxygenates in lower-oxygen content, formate-assisted pyrolysis oils (FAsP). Ru catalysts with a wide range of dispersion on carbon, silica, alumina, and titania supports were synthesized, characterized and evaluated for hydrodeoxygenation (HDO) activity using phenol as a model compound. Metal content, phase, and particle size were determined with ICP-OES, EXAFS/XANES, and CO pulse chemisorption, respectively. High dispersion of ruthenium on the supports converts more phenol to products. The majority of catalysts predominantly catalyze the hydrogenation (HYD) route typical of noble metal catalysts. A highly dispersed Ru/TiO₂ catalyst shows unusually high selectivity toward direct deoxygenation (DDO) and outstanding activity. We suggest that the DDO pathway on titania involves a bifunctional catalyst, where hydrogen creates reduced titania sites, created by hydrogen spillover, that interact strongly with the phenol hydroxyl group.

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1. Introduction

Hydrodeoxygenation (HDO) is a class of reactions utilized to upgrade the quality of biofuels, typically involving heating pyrolysis oil to 573–873 K under high pressures of hydrogen over a heterogeneous catalyst [1–12]. Early HDO attempts used catalysts and reactor conditions from hydrodesulfurization and hydrodenitrogenation processes developed for the treatment of petroleum feeds [9,13] to limit SO_x and NO_x emissions [14]. Recent HDO experiments have incorporated a wide variety of active metals

(Ru [2,15], Pd [16–18], Mo [2], Pt [15,16]), metal phosphides [19–21] and catalyst frameworks, (active carbon [2,15,17] mesoporous silicas [18,22,23], zeolite [17] and alumina [15]). These recent approaches are preferable to traditional hydrotreatment catalysts (sulfided NiMo/Al₂O₃ and CoMo/Al₂O₃) because they do not introduce sulfur into the manufacturing process with the concomitant risk of contaminating a naturally sulfur-free fuel [15]. Recent advances have been reviewed, and while model compound studies have identified reaction networks, a fundamental understanding of reaction mechanisms, kinetics, and the nature of the active sites is still lacking [24].

Recently, our group has developed a new pyrolysis process called formate-assisted pyrolysis (FAsP) involving co-feeding of biomass and formate salts [25–28] that results in oxygen contents of about 8%, compared to 40–45% in conventional bio-oils [29–33]. Chemical analysis shows that while the oxygen content is greatly improved, the FAsP oils remain rich in substituted phenols [27,28]. Thus, for FAsP oils specifically, and bio-oils more generally, the ability to upgrade phenolic compounds is critical.

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Substituted phenols like guaiacol [34–40] are readily converted to phenol or catechol under traditional upgrading processes, but the catalytic conversion of phenol to an oxygen-free compound is difficult [41,42] as the C–O bond in phenol is among the more difficult bonds to cleave in bio-oils [24,43–45]. Phenol also provides a useful probe of the catalytic reaction mechanisms, specifically providing insight into whether hydrogen used in the reaction is being directed towards hydrogenation or direct deoxygenation.

In this report, we present data on a series of supported Ru catalysts designed for the hydrodeoxygenation of fast pyrolysis oils. We correlate variations in activity and selectivity for reactions of phenol with physical properties of the catalysts.

2. Experimental

2.1. Materials and methods

Hydrochloric acid (HCl, 37%), ruthenium (III) chloride hydrate ($\text{RuCl}_3 \cdot x\text{H}_2\text{O}$), tetraethylorthosilicate (TEOS, 99.999%), carbon nanofibers (CNF, iron free, graphitized, conical, >99%), Ru on carbon (Ru/C, 5 wt%) and Ru on alumina ($\text{Ru}/\text{Al}_2\text{O}_3$, 5% Ru basis) were obtained from Sigma-Aldrich. A 5% Ru on carbon was also obtained from Strem. Poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) ($M_r = 5750$, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Pluronic P123) was obtained from BASF. Liquified phenol (>89%, ~10% H_2O) was obtained from Fischer Scientific. Silica gel granules (SG, silica gel no. 646, 35–60 mesh) were obtained from W.R. Grace & Co. MCM-41 was received as a generous gift from Martin Piech when he was in the Yale University Department of Chemical Engineering. SG, MCM-41 and CNF supports were impregnated as received. Titanium dioxide P25 was purchased from Degussa. NORIT activated carbon support was used for the synthesized Ru/C catalyst. Aluminum oxide support was purchased from Acros Organics. Reference standards for X-ray absorption spectroscopy (XAS) measurements, Ru powder (Mesh 22), $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, RuO_2 , and $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ were obtained from Sigma-Aldrich. All materials in this work were used without further purification.

2.2. Catalyst synthesis and impregnation

SBA-15 was synthesized following a modified literature procedure, as described previously [46]. Two different metal impregnation approaches were used. All catalyst supports were oven dried prior to impregnation.

For porous silica supports, MCM-41, SBA-15 and silica gel (SG), incipient wetness impregnation [47–50], [51] (IWI) was used following a modified IWI literature procedure [51]. A solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, calculated to theoretical metal loadings ranging from 0.5 to 10 wt%, was prepared in a total pore volume (TPV) equivalent of H_2O . The solution was added dropwise to each support and left to age overnight. Samples were then dried in air overnight at 353 K. Those used at this stage were designated as (U) for uncalcined. Selected catalysts were calcined in air at 873 K for 8 h using a ramp rate of 1 K/min and designated as (C) for calcined.

For low porosity CNF, TiO_2 , Al_2O_3 , and C supports, wetness impregnation (WI) was employed following a modified literature procedure [47]. A solution of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ (35 mL) was prepared to attempt to achieve a final metal loading near 5 wt%. The solution was added dropwise to the support and aged overnight. The catalyst was then dried at 383 K for 20 h. Selected catalysts were calcined in air at 473 K for 4 h using a ramp rate of 1 K/min.

In summary, the following catalysts were either purchased or synthesized and studied in this report: Carbon-based supports: Ru/C from Strem, Ru/C from Acros, Ru/C-U (synthesized uncalcined), Ru/CNF; Silica-based supports: Ru/SBA-15, Ru-SG,

Ru/MCM-41 (low metal content), Ru/MCM-41 (medium metal content), Ru/MCM-41 (high metal content), Ru/MCM-41-U (uncalcined) Alumina-based supports: $\text{Ru}/\text{Al}_2\text{O}_3$ (SA) (purchased from sigma aldrich), $\text{Ru}/\text{Al}_2\text{O}_3$ -U (synthesized uncalcined); Titania-based supports: Ru/TiO_2 , Ru/TiO_2 -U (uncalcined). All synthesized catalysts were calcined unless specified.

2.3. Catalyst characterization

2.3.1. N_2 porosimetry

Nitrogen sorption isotherms were determined at 77 K using a Micromeritics ASAP-2020 instrument. Surface area, total pore volume and pore size calculations were performed using standard approaches. Surface area was calculated from the BET plot [52], total pore volume (TPV) was obtained from the single point adsorption volume at $P/P_0 = 0.995$, and the average pore size reported is the average adsorption branch BJH [53] pore diameter (4 V/A), using the KJS [54] correction.

2.3.2. Metal determination

Ru content analysis was performed by Galbraith Laboratories or done using a Thermo Scientific iCAP 600 ICP-OES spectrometer with microwave-assisted digestion.

2.3.3. X-ray absorption fine structure spectroscopy

For the characterization of the local electronic and atomic structure of Ru in the catalysts, we performed synchrotron based X-ray absorption spectroscopy (XAS) measurements at the bend magnet beamline X18B at the National Synchrotron Light Source, Brookhaven National Laboratory. The as prepared (calcined or uncalcined) powder catalyst samples were pressed into solid pellets (~150 mg in pellets of ~10 mm dia, pressure 6 tons) and loaded into a Nashner-Adler reactor for *in situ* transmission studies. Catalysts were reduced using 5% H_2 /He flow while heating at a ramp rate of 20 K/min to 673 K. Reduction occurred during the first 15 min of the temperature ramp, between 500 and 650 K. The catalysts were held at the final temperature for 4 h, although no further changes were observed. Passivation was performed at room temperature under 5% O_2 /He flow. The reduction and passivation processes were monitored *in situ* during the temperature ramp using X-ray absorption near edge structure (XANES) spectroscopy, while the extended X-ray absorption fine structure (EXAFS) was measured for each sample at the completion of the chemical reaction (i.e. at steady state). Three ion gas chambers were used to record in transmission mode, the incident (filled with Ar/He), transmitted (filled with Ar/Kr), and reference (filled with Ar/He) beam. A Ru foil was placed after the second ion chamber as both an energy calibration (Ru K-edge: 22.1 keV) as well as a reference XANES/EXAFS spectrum for direct comparison to the catalytic samples. Four scans were taken and subsequently averaged during data processing. Reference spectra were measured for Ru, $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, RuO_2 , and $\text{RuO}_2 \cdot x\text{H}_2\text{O}$ and are provided in the supplemental material.

2.3.4. EXAFS analysis

Data processing and analysis was done using the Horae [55] suite of IFEFFIT programs [56]. Initial estimates of the threshold energy values (E_0) were obtained via the inflection point in the normalized absorption edges. A Hanning window was applied to a selected k -range (nominally $3 \text{ \AA}^{-1} < k < 14 \text{ \AA}^{-1}$) to obtain high quality Fourier transformed EXAFS data. Fitting of the Ru foil standard led to a passive electron reduction factor (S_0^2) of 0.77, where this value was fixed for the analysis of the catalyst samples. Using a Ru bulk metal (hcp) chemical model, FEFF6 was used [57] to calculate the

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