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#### Hydrodeoxygenation of guaiacol on tungstated zirconia supported Ru catalysts

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#### Graphical abstarct



#### Highlights

- Ru nanoparticles supported on tungsten-added zirconia
- Hydrodeoxygenation of guaiacol using using Ru/W/ZrO<sub>2</sub> bifunctional catalyst.
- Catalytic activity depending on the Ru particle size.
- Ru particle size depending on the combination of acidity and WO<sub>x</sub> particles.

#### Abstract

Ru nanoparticles supported on tungstated zirconia (WZr) were prepared and used for the catalytic hydrodeoxygenation of guaiacol to deoxygenated hydrocarbon fuels. The tuning of tungsten, from 5 to 20 wt%, adjusted the number of acid sites on the tungstated zirconia and the size of the Ru nanoparticles. The optimum fraction of tungsten was determined for the optimum hydrodeoxygenation activity. The conversion of guaiacol reached a maximum of 96.8% for 10 wt% of tungsten. Increasing the tungsten fraction increased the number of acid sites and the

dispersion of Ru, but the formation of tungsten oxide  $(WO_x)$  particles with too large a fraction of tungsten inhibited the formation of smaller Ru nanoparticles, thus reducing the catalytic activity.

Keywords: tungstated zirconia, ruthenium, guaiacol, biomass, lignin, hydrodeoxygenation

#### **1. Introduction**

Metal nanoparticles on solid acids exhibit the bifunctional catalytic properties of hydrogen adsorption on metals and the defunctionalization of substrates on solid acids, and these characteristics are required for the hydrodeoxygenation (HDO) of oxygenates [1-3]. The proximity of metal nanoparticles and solid acids may have additional synergistic effects on the catalytic activity [4,5] which can be predetermined when designing acid-supported nanoparticle catalysts. A lot of multifunctional or bifunctional catalysts composed of more than one active component have been reported. Noble metal nanoparticles supported on solid acids attributed to hydrogen adsorption during the HDO reaction; rhodium and ruthenium were found to exhibit high HDO activity in our previous study [1-3,6]. The acidic supports manipulate the HDO reaction pathway and the product distributions [1,7], which determine the activity of the HDO catalysts by adjusting the dehydration or other deoxygenation processes.

Renewable biomass has been studied as a resource for the manufacturing of sustainable fuels and fine chemicals [8] without increasing atmospheric CO<sub>2</sub> [9]. The liquid oils, or bio-oils, obtained by thermolysis processes including pyrolysis [10,11] and hydrothermal liquefaction [12,13] are used as feedstocks for hydrodeoxygenation. Because of their of oxygen atoms, bio-oils require deoxygenation if they are to be used as petroleum-like fuels and chemicals [14]. Hydrodeoxygenation (HDO) is a process which stabilizes and upgrades oxygenated reactants; this process involves hydrogenation using hydrogen-adsorbed metals and deoxygenation using a solid acid support [1,15].

In this study, the strong solid acid tungstated zirconia (WZr) is selected as an acidic support for the HDO catalysts [16,17], which has been previously used for esterification [18-20], the dehydration of glycerol [21-23], the isomerization of alkanes [24,25], and the conversion of cellulose [26]. The surface density of tungsten oxide (WO<sub>x</sub>) adjusts the surface acidity of the catalysts by creating Brønsted acid sites [16] and a crystallographic phase [27]. WO<sub>x</sub> also creates strong interaction between deposited metals and WO<sub>x</sub>, promoting aqueous-phase HDO activity [16,17]. Detailed information about the synergy between the components is not yet available. We performed the HDO reaction of the bio-oil model guaiacol using Ru nanoparticles supported on W/ZrO<sub>2</sub> or Ru/WZr. The goal of this study is to understand the interaction between the metal and the acidic W/ZrO<sub>2</sub> and to determine the effects of the interaction on the HDO reaction pathway. This understanding should help in the development of more efficient bifunctional catalysts.

#### 2. Experimental

#### 2.1. Materials

All chemicals were used without further purification unless indicated otherwise. 4-Methylcyclohexanol (98%) was purchased from TCI (Tokyo, Japan). Methylcyclohexane (99%), cyclohexane (99%), cyclohexanone (99.8%), cyclohexanol (99%), cyclohexene (99%, inhibitorfree), guaiacol (99%), and ammonium metatungstate hydrate (99.99%) were purchased from Aldrich (Milwaukee, WI, USA). Zirconium oxychloride octahydrate was purchased from Kanto Chemical (Tokyo, Japan). 2-Methoxycyclohexanol (97%) and ruthenium (III) chloride (RuCl<sub>3</sub>, anhydrous) were purchased from Alfa (Ward Hill, MA, USA). Tungstated zirconia was obtained

from Wako Pure Chemical Industries, Ltd. (Osaka, Japan).

#### 2.2. Preparation of catalysts

#### 2.2.1. Preparation of tungstated zirconia and other supports

Zirconium oxyhydroxide was prepared by hydrolysis of 0.5 M zirconium oxychloride solution using the drop wise addition of aqueous ammonia solution (28%) to a final pH of 10. The precipitate was filtered and washed with deionized water to remove chloride ions. The obtained zirconium oxyhydroxide was then dried at 120 °C for 12 h and ground in an agate mortar to obtain well-powder and homogenized sample. A series of tungstated zirconia catalysts were prepared by hydrothermal impregnation of zirconium oxyhydroxide with aqueous solutions of ammonium metatungstate to yield nominal tungsten loadings of 5, 10, 15, and 20 wt%. The resulting slurries were stirred for 30 min at room temperature and put in the autoclave at 180 °C for 12 h. The slurries were then evaporated in vacuum condition to dryness at 70 °C, and subsequently calcined in air at a temperature of 800 °C for 2 h. The resulting powdered solids were designated xWZr(syn), where x is the nominal bulk tungsten loading.  $ZrO_2$  without W (ZrO<sub>2</sub>(syn), ZrO<sub>2</sub> prepared in our lab) was also prepared by calcination of zirconium oxyhydroxide in air at temperature of 800 °C for 2 h. Tungsten oxide was also prepared by calcination of ammonium metatungstate in air at temperature of 800 °C for 2 h. For comparison, Mo-deposited ZrO<sub>2</sub> (MoZr) and V-deposited ZrO<sub>2</sub> (VZr) were also prepared as supports. Mo and V were loaded on zirconium oxyhydroxide by the above-mentioned method with aqueous solution of ammonium heptamolybdate and ammonium metavanadate to yield nominal Mo and V loadings of 15 wt%. In addition, tungstated zirconia was also prepared by wet impregnation of

zirconium oxyhydroxide with aqueous solutions of ammonium metatungstate to yield nominal W loading of 15 wt%. The resulting slurries were stirred at room temperature for 12 h. The slurries were then evaporated in vacuum condition to dryness at 70 °C, and subsequently calcined in air at a temperature of 800 °C for 2 h. The prepared catalyst was designated as WZr(imp).

2.2.2. Preparation of supported ruthenium catalysts.

Ruthenium (5 wt-%) loadings were prepared by wet impregnation method using ruthenium(III) chloride hydrate as precursor. Prior to impregnation, the support powders were sieved to obtain particles smaller than 150  $\mu$ m. The impregnated catalysts were calcined under air flow at 400 °C for 2 h, and reduced in a flow of 5% H<sub>2</sub>/Ar at 400 °C for 4 h. The prepared catalysts were passivated with a flow of 0.5% O<sub>2</sub>/N<sub>2</sub> at room temperature for 30 min and stored under ambient conditions [1].

#### 2.3. Characterizations of catalysts

TEM images of the prepared catalysts were obtained using a Tecnai G2 F20 at 200 kV. Ammonia temperature-programmed desorption (NH<sub>3</sub>-TPD) measurements were performed to confirm the acidity of the catalysts. Approximately 50 mg of catalyst was placed in a quartz reactor and saturated with ammonia at 100 °C. The desorbed NH<sub>3</sub> was measured using a TCD while the catalyst was heated from 100 to 700 °C at a heating rate of 10 °C/min in He flow (30 mL/min). Powder X-ray diffraction (powder XRD) results were obtained using a Rigaku X-ray diffractometer with a CuK $\alpha$ 1 ( $\lambda$  = 0.15406 nm) radiation source operated at 40 kV and 30 mA. N<sub>2</sub>-physisorption was performed using a Micromeritics ASAP 2020 instrument, with samples

degassed at 120 °C for 2 h prior to recording adsorption/desorption isotherms. The total surface area and pore volume were determined using the BET (Brunauer-Emmett-Teller) equation. The pore size distribution (PSD) curves were calculated by BJH (Barrett–Joyner–Halenda) method. X-ray photoelectron spectroscopy (XPS) results for the prepared catalysts were recorded on a PHI 5000 VeraProbe spectrometer (ULVAC-PHI), and the obtained spectra were calibrated using C 1s at 284.6 eV. Raman spectra analysis was performed at National Center for Inter-University Research Facilities (Seoul, Korea) using a T64000 Triple Raman Spectrometers (HORIBA Scientific). CO-chemisorption was performed using a BELCAT-B catalyst analyzer. The catalyst powder (30 mg), after being placed in a U-shaped quartz reactor, was heated under He flow (50 mL/min) to 350 °C at a rate of 10 °C/min. This was followed by H2 treatment at 350 °C for 1 h. The powder was then cooled to 50 °C under He flow (50 mL/min) and further treated at 50 °C for 30 min in order to clean the metal surface of the residual adsorbed hydrogen. The powder was subsequently exposed to pulses of 10% (v/v) CO/He at 50 °C under He flow (30 mL/min). The number of active-surface metal atoms was calculated from the measured CO concentrations of the effluent gas.

#### 2.4. Catalytic HDO of guaiacol

The hydrodeoxygenation of guaiacol was performed in a stainless steel autoclave reactor (volume: 110 mL). In a typical reaction procedure, guaiacol (8.96 mmol), water (29 mL), and a solid catalyst (20 mg) were added to the reactor. After flushing with  $N_2$  gas, the reactor was pressurized to 40 bar with  $H_2$  at room temperature. The reaction was performed at 270 °C for 1 h at an agitation rate of 800 rpm. The reactor was heated from room temperature to 270 °C at a rate

of 4 °C/min. After the reaction, the reactor was cooled to room temperature and the mixture was extracted with ethyl acetate. The catalyst powder was removed and the liquid product was collected. The extracted products were identified using a gas chromatograph–mass spectrometer combination (GC/MS, Agilent 7890A with 5975C inert MS XLD) with an HP-5MS capillary column (60 m × 0.25 mm × 250  $\mu$ m); products were further quantified using a gas chromatograph with an HP-5 capillary column (60 m × 0.25 mm × 250  $\mu$ m) equipped with a flame ionized detector (GC/FID, HP Chemstation Series II 5890) using ethyl guaiacol as an internal standard.

The complex mixture of the products obtained from guaiacol was classified into three groups, which were compounds containing no oxygen atoms (0-Os), those containing one oxygen atom (1-Os), and those containing two oxygen atoms (2-Os). The 0-Os included cyclopentane, methylcyclopentane, and cyclohexane. The major 1-O compounds included cyclohexanol, cyclohexanone, cyclopentanemethanol, methoxybenzene, and phenol. 2-Methoxycyclohexanol, 1,2-cyclohexanediol, and 1,2-benzenediol were the major compounds of the 2-Os group. Conversion of guaiacol (X<sub>GUA</sub>), product yields (Y<sub>i</sub>), and product selectivity (S<sub>i</sub>) were calculated as follows:

Conversion 
$$(X_{GUA}, \%) = \frac{n_{GUA}^0 - n_{GUA}^f}{n_{GUA}^0} \cdot 100$$
  
Yield  $(Y_i, \%) = \frac{n_i}{\frac{m_i}{m_{GUA}}} \cdot 100$   
Selectivity  $(S_i, \%) = \frac{Y_i}{X_{GUA}} \cdot 100$ 

where  $n_{GUA}^0$  is the initial amount of guaiacol (mmol),  $n_{GUA}^f$  is the final amount of guaiacol

(mmol),  $n_i$  is the amount of i-product in the liquid phase (mmol), and  $m_i$  and  $m_{GUA}$  are the stoichiometric coefficients in the reaction of guaiacol conversion to i-product.

#### 3. Results and discussion

#### 3.1. Effects of preparation methods on the catalytic activity

The catalytic activity of WZr-supported Ru catalysts prepared by different methods was studied to understand the effects of how these catalysts are prepared on their activity. Based on our previous study, Ru metal was selected as the best precious metal catalyst for hydrodeoxygenation [1-3]. Two different types of WZrs were prepared in our lab, as described in the experimental section: (i) WZr(syn) was prepared by the hydrothermal impregnation of tungsten into zirconia prepared in our lab, and (ii) WZr(imp) was prepared by the wet impregnation of tungsten, at room temperature, to zirconia, also prepared in our lab. X-ray diffraction measurements exhibited that both supports had similar structures (Fig. S1). Ru/WZr(syn) exhibited much better activity than Ru/WZr(imp) (Table 1). Replacing tungsten, Mo-deposited ZrO<sub>2</sub> (WZr) and V-deposited ZrO<sub>2</sub> (VZr) were also used as supports; these materials also exhibited catalytic activity, although the fully deoxygenated products formed only to a lesser extent.

(Table 1)

Spent Ru/WZr was used for the recyclability test (Fig. S2). Although the conversion of guaiacol decreased from 98.5 to 86.7% and the selectivity to 0-Os decreased from 49.8 to 43.7% during

the third run, a significant decrease in the activity was not observed. The decreasing activity of the spent catalysts could be attributed to the decreasing number of active sites of ruthenium. Ru dispersion measured by CO-chemisorption decreased from [CO]/[Ru] = 0.087 (fresh catalyst) to 0.036 (after the third run).

3.2. Characterization of Ru/WZr(syn) depending on the quantity of tungsten.

The crystal structures of xWZr(syn) were observed with X-ray diffraction (XRD) (Fig. 1). Without adding tungsten, only the monoclinic ZrO<sub>2</sub> formed [28]. With the addition of 5 wt% W, the diffraction peaks of tetragonal ZrO<sub>2</sub> appeared. An additional addition of tungsten increased the intensity ratio of the diffraction peaks of monoclinic and tetragonal ZrO<sub>2</sub>, which indicated that the formation of tetragonal ZrO<sub>2</sub> was preferred with the addition of tungsten, as was reported for doped ZrO<sub>2</sub>, which exhibited cubic or tetragonal structures [28]. In the presence of tungsten oxide (WO<sub>x</sub>) species after impregnation, metastable tetragonal ZrO<sub>2</sub> crystallites were stabilized during calcination in air at 800 °C. WO<sub>x</sub> species strongly influence the formation of zirconium oxyhydroxide crystallization into ZrO<sub>2</sub> [29]. As a result, the fraction of tetragonal ZrO<sub>2</sub> contents was increased by increasing the W loading amount.

(Fig. 1)

The chemical structures of WZr(syn) were further observed using Raman spectroscopy (Fig. 2). The peak at 952 cm<sup>-1</sup>, indicating the formation of isolated/polymeric surface mono-oxo W=O species, increased when increasing the amount of tungsten added, which confirmed the formation

of WO<sub>x</sub> particles from the highly dispersed tungsten atoms on the ZrO<sub>2</sub> surface, although the formation of WO<sub>x</sub> particles was not confirmed in the XRD results (Fig. 1). The formation of O-W-O, which was confirmed by the presence of the 806 and 713 cm<sup>-1</sup> peaks of the WO<sub>3</sub> reference, was not observed for WZr(syn). These bands correspond to well-ordered WO<sub>3</sub> nanoparticles [30]. With an increase in the quantity of tungsten, the peak of tetragonal ZrO<sub>2</sub> at 490 cm<sup>-1</sup> also increased, as also confirmed by the XRD analysis. Peaks of W=O at 952 cm<sup>-1</sup> and tetragonal ZrO<sub>2</sub> at 490 cm<sup>-1</sup> were not observed for the WO<sub>3</sub> reference, indicating that tungsten did not form isolated well-ordered WO<sub>3</sub> nanoparticles on WZr(syn) for additions of up to 20 wt% of tungsten and that the formation of tetragonal ZrO<sub>2</sub> is attributable to the addition of tungsten to ZrO<sub>2</sub>. The formation of tungsten agglomerates or WO<sub>x</sub> particles with increasing quantities of tungsten was further observed for Ru/15WZr(syn), tiny agglomerates of tungsten were also observed, confirming the Raman spectra observations.

(Fig. 2)

(Fig. 3)

While the formation of WO<sub>x</sub> particles occurred after increasing the quantity of tungsten, the electronic structures of Ru and W with different fractions of tungsten were observed using X-ray photoelectron spectroscopy (Fig. 4). For the Ru 3d peaks, only Ru 3d<sub>5/2</sub> peaks were analyzed because Ru 3d<sub>3/2</sub> overlapped C 1s at 284.6 eV. The peak locations of Ru 3d<sub>5/2</sub> were red-shifted by approximately 0.5 eV from 280.1 to 279.6 eV with an increase in the quantity of tungsten. When

a large quantity of tungsten was deposited, Ru became more electron-rich, which may improve the hydrogenation activity by electron back-donation to dissociate hydrogen molecules. Both cationic (shoulder at approximately 281 eV) and metallic (at 280.1 eV) Ru peaks were observed because Ru nanoparticles were exposed to air after the preparation of the catalyst. For the W 4f peaks, both W 4f<sub>5/2</sub> and W 4f<sub>7/2</sub> peaks, which were attributed to W<sup>6+</sup> surface species and W<sup>5+</sup> surface species from tungsten species on the surface of ZrO<sub>2</sub>, did not significantly change with an increase in the quantity of tungsten, although the intensity increased. Small shifts in the W 4f peaks towards higher binding energy, caused by the greater formation of polytungstate clusters on the zirconia surface, as confirmed by a Raman analysis [20], were observed for both the 15WZr and 20WZr samples.

(Fig. 4)

The acidity of WZr(syn) was measured using NH<sub>3</sub>-TPD (Fig. 5 and Table 2). With an increase in the amount of tungsten added, the acidity increased from 0.017 (ZrO<sub>2</sub>(syn)) to 0.834 mmol/g (20WZr(syn)), although isolated WO<sub>3</sub> (no ZrO<sub>2</sub>) exhibited negligible acidity. These observations indicate that the highly distributed tungstate species in the form of monomeric or polymeric tungstate species and not WO<sub>3</sub> crystallites[31] increased the acidity of WZr(syn) [32,33].

(Fig. 5)

(Table 2)

Because the surface area of the catalysts is one of the most important descriptors used to determine the catalytic activity, the pore structures were observed using N<sub>2</sub>-physisorption (Table 2). ZrO<sub>2</sub>(syn) showed a low BET surface area of 9.8  $m^2/g$ , likely attributable to the formation of monoclinic crystal from zirconium oxyhydroxide [19]. The addition of W to ZrO<sub>2</sub> significantly increased the surface area of the catalysts. WZr(syn) exhibited BET surface area which ranged from 34.9 - 52.3  $m^2/g$  and a negligible micropore surface area. The increase in the surface area was caused by the strong interaction of W with ZrO<sub>2</sub>, which reduces the surface diffusion of ZrO<sub>2</sub>, inhibits sintering, and stabilizes the tetragonal phase of ZrO<sub>2</sub>, leading to an increase in the surface area [34]. The fraction of tetragonal ZrO<sub>2</sub> compared to monoclinic ZrO<sub>2</sub> increased with an increase in the concentration of tungsten, but it is not clear as to whether the acidity is related to the crystal structure, although the possible dependence of the acidity on the crystal structure cannot be dismissed. The dispersions of Ru nanoparticles supported on ZrO<sub>2</sub>(syn), WZr(syn), and WO<sub>3</sub> were measured using CO-chemisorption (Table 2). Similar to our previous works [2,6,35], the dispersions of Ru nanoparticles for all catalysts were relatively low. In addition, the results indicated that WZr(syn) with less tungsten added (5WZr(syn) and 10WZr(syn)) allowed a larger dispersion of Ru, although the BET surface areas of 5WZr(syn) and 10WZr(syn) were not larger.

Based on the observations in Table 2, the acidity per surface area and the fraction of tetragonal ZrO<sub>2</sub> were correlated with the surface density of tungsten on ZrO<sub>2</sub> (Fig. 6). The acidity (per surface area) appears to increase with an increase in the surface density of tungsten, indicating that the coupling of highly dispersed tungsten and ZrO<sub>2</sub> produced acid sites [32,33], as confirmed by the Raman spectroscopy analysis. The formation of tetragonal ZrO<sub>2</sub>, which has been reported

to be catalytically active in many reactions frequently with the help of dopants [36,37], appears to occur because of the addition of W, but the fraction of tetragonal ZrO<sub>2</sub> did not significantly increase with an increase in the tungsten density, indicating that the nucleation of tetragonal ZrO<sub>2</sub> was initiated with a small quantity of tungsten and that a further addition of tungsten did not significantly affect the formation of tetragonal ZrO<sub>2</sub>.

#### (Fig. 6)

The characterizations of Ru/xWZr(syn) indicated the following: (i) tungsten is well distributed on the surface of  $ZrO_2$  when its fraction is small, but it forms isolated  $WO_x$  particles with an increase in the quantity of tungsten; (ii) supported Ru nanoparticles become more electron-rich as the quantity of tungsten increases; and (iii) surface acid sites are created by the addition of tungsten, and their quantity of these sites is proportional to the quantity of the deposited tungsten.

3.3. Catalytic activity of Ru/WZr(syn) depending on the quantity of tungsten.

Based on the characterization results, the hydrodeoxygenation of guaiacol, the process of which requires both acidity and hydrogen adsorption [1-3,6,38], was to correlate the catalytic activity of Ru/xWZr(syn) with its structure (Fig. 7 and Table S1). With an increase in the conversion of guaiacol, the yield of 0-Os increased while those of 1-Os decreased, indicating that the deoxygenation of guaiacol occurs upon the hydrogenation active sites on the catalysts (Fig. S3). The conversion of guaiacol increased as the amount of W increased, but it reached a maximum

of 96.8% for Ru/10WZr(syn) and decreased with a further addition of W. This indicates that the conversion of Ru/xWZr(syn) was optimized for Ru/10WZr(syn). Similar results were observed when the reaction was performed at a lower temperature (Fig. S4). The conversion of guaiacol was highly affected by the dispersion of Ru, [CO]/[Ru], as described in Table 2 and Fig. 8. Highly dispersed Ru particles can facilitate the adsorption of hydrogen atoms, improving the hydrogenation of guaiacol and its derivatives, following the reported reaction pathway [1]. Compared to the conversion of guaiacol, the selectivity of deoxygenated products, represented by 1-Os in this study, was not determined by the acid sites; this point is different from observations in our previous reports [1,38] but supports our recent work, which has emphasized the dispersion of metal [2]. Although the dispersion of Ru appears to determine the HDO activity, both the conversion of guaiacol and the selectivity to 0-Os reached maximum levels at [CO]/[Ru] = 0.048 (Ru/10WZr(syn)) and decreased at [CO]/[Ru] = 0.063 (Ru/5WZr(syn)). We believe that the quantity of acid sites slightly affected the catalytic activity because more active Ru/10WZr(syn) has more acid sites than less active Ru/5WZr(syn) does, although the effects of Ru dispersion are more important.

(Fig. 7)

(Fig. 8)

While the combination of metal nanoparticles and an acidic support is important when preparing highly active catalysts for the hydrodeoxygenation process, the optimized complex of Ru nanoparticles and acidic WZr appears to exhibit high activity. Increasing the number of acid sites

is known to increase the dispersion of metal nanoparticles. This study also demonstrated that the Ru dispersions of Ru/ZrO<sub>2</sub>(syn), Ru/5WZr(syn), and Ru/10WZr(syn) increased with an increase in the quantity of acid sites (Table 2 and Fig. 8). The Ru dispersion, however, decreased for Ru/15WZr(syn) and Ru/20WZr(syn) despite the fact that the acidity of these supports are greater. Based on the results described in Table 2 and Fig. 8, we formed a hypothesis regarding the effects of tungsten on ZrO<sub>2</sub> on the Ru dispersion, as depicted in Fig. 9. An increase in the quantity of acid sites with an increase in the quantity of tungsten increased the Ru dispersion or the number of Ru active sites, but too large a quantity of tungsten appears to inhibit the formation of smaller Ru nanoparticles (Fig. 9). Increasing the fraction of tungsten produced WO<sub>x</sub> particles (Fig. 2) which did not favor the deposition of Ru nanoparticles. Therefore, Ru nanoparticles, for which smaller ZrO<sub>2</sub> spaces for their deposition were observed, became larger with the formation of WO<sub>x</sub>, which occupied the ZrO<sub>2</sub> surface. Although increasing the quantity of tungsten improved the formation of acid sites, the decreasing number of Ru nanoparticles with the formation of WO<sub>x</sub> decreased the catalytic HDO activity. The highly dispersed tungsten with the smaller fraction of tungsten and the blocking of the ZrO<sub>2</sub> surface because of WO<sub>x</sub> particles with the larger fraction of tungsten modified the size of the Ru nanoparticles and thus adjusted the HDO activity.

(Fig. 9)

#### 4. Conclusion

Ru nanoparticles supported on tungstated-zirconia were prepared and their hydrodeoxygenation

activity was observed. The acidity created by highly dispersed tungsten produced smaller Ru nanoparticles with larger surface Ru atoms, improving the catalytic hydrodeoxygenation activity. In contrast, the formation of  $WO_x$  large addition of tungsten inhibited the formation of highly dispersed Ru particles, which reduced the hydrodeoxygenation activity. As a result of these observations, it can be said that an optimum fraction of tungsten to modify the acidity and the Ru dispersion does exist and can be used to achieve the optimal catalytic hydrodeoxygenation activity.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

#### References

- [1] C.R. Lee, J.S. Yoon, Y.-W. Suh, J.-W. Choi, J.-M. Ha, D.J. Suh, Y.-K. Park, Catal. Commun., 17 (2012) 54-58.
- [2] A.A. Dwiatmoko, L. Zhou, I. Kim, J.-W. Choi, D.J. Suh, J.-M. Ha, Catal. Today, 265 (2016) 192-198.
- [3] J.S. Yoon, J.-W. Choi, D.J. Suh, K. Lee, H. Lee, J.-M. Ha, ChemCatChem, 7 (2015) 2669-2674.
- [4] I. Yati, M. Ridwan, G.E. Jeong, Y. Lee, J.-W. Choi, C.W. Yoon, D.J. Suh, J.-M. Ha, Catal. Commun., 56 (2014) 11-16.
- [5] I. Yati, A.A. Dwiatmoko, J.S. Yoon, J.-W. Choi, D.J. Suh, J. Jae, J.-M. Ha, Appl. Catal., A, 524 (2016) 243-250.
- [6] A.A. Dwiatmoko, S. Lee, H.C. Ham, J.-W. Choi, D.J. Suh, J.-M. Ha, ACS Catal., 5 (2015) 433-437.
- [7] A. Foster, P.M. Do, R. Lobo, Top. Catal., 55 (2012) 118-128.
- [8] R.A. Sheldon, Green Chem., 16 (2014) 950-963.
- [9] F. Orecchini, E. Bocci, Energy, 32 (2007) 1006-1011.
- [10] C. Liu, H. Wang, A.M. Karim, J. Sun, Y. Wang, Chem. Soc. Rev., 43 (2014) 7594-7623.
- [11] J. Choi, J.-W. Choi, D.J. Suh, J.-M. Ha, J.W. Hwang, H.W. Jung, K.-Y. Lee, H.-C. Woo, Energy Convers. Manage., 86 (2014) 371-378.
- [12] H.-S. Lee, J. Jae, J.-M. Ha, D.J. Suh, Bioresour. Technol., 203 (2016) 142-149.
- [13] H.-S. Lee, H. Lee, J.-M. Ha, J. Kim, D.J. Suh, Industrial Crops and Products, 76 (2015) 104-111.
- [14] T. Sundqvist, A. Oasmaa, A. Koskinen, Energy Fuels, 29 (2015) 2527-2534.
- [15] Q. Zhang, J. Chang, T. Wang, Y. Xu, Energy Convers. Manage., 48 (2007) 87-92.
- [16] O.G. Marin-Flores, A.M. Karim, Y. Wang, Catal. Today, 237 (2014) 118-124.
- [17] C. Liu, J. Sun, H.M. Brown, O.G. Marin-Flores, J.T. Bays, A.M. Karim, Y. Wang, Catal. Today, (2015).
- [18] D.E. Lopez, J.G. Goodwin, D.A. Bruce, S. Furuta, Appl. Catal. A, 339 (2008) 76-83.
- [19] D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Goodwin, J. Catal., 247 (2007) 43-50.
- [20] V.C. dos Santos, K. Wilson, A.F. Lee, S. Nakagaki, Appl. Catal., B, 162 (2015) 75-84.
- [21] S.R. Ginjupalli, S. Mugawar, N.P. Rajan, P.K. Balla, V.R.C. Komandur, Appl. Surf. Sci., 309 (2014) 153-159.
- [22] S.H. Chai, B. Yan, L.Z. Tao, Y. Liang, B.Q. Xu, Catal. Today, 234 (2014) 215-222.
- [23] S.H. Chai, L.Z. Tao, B. Yan, J.C. Vedrine, B.Q. Xu, Rsc Adv, 4 (2014) 4619-4630.
- [24] J.M. Hidalgo, D. Kaucky, O. Bortnovsky, R. Cerny, Z. Sobalik, Rsc Adv, 5 (2015) 56625-56628.
- [25] J.E. Bruno, K.M. Dooley, Appl. Catal. A, 497 (2015) 176-183.
- [26] F. Chambon, F. Rataboul, C. Pinel, A. Cabiac, E. Guillon, N. Essayem, Appl. Catal. A, 504 (2015) 664-671.
- [27] Y.K. Hong, D.W. Lee, H.J. Eom, K.Y. Lee, Appl. Catal. B, 150 (2014) 438-445.
- [28] C.J. Howard, R.J. Hill, B.E. Reichert, Acta Crystallogr. Sect. B: Struct. Sci., 44 (1988) 116-120.
- [29] D.G. Barton, S.L. Soled, G.D. Meitzner, G.A. Fuentes, E. Iglesia, J. Catal., 181 (1999) 57-72.

[30] E.I. Ross-Medgaarden, W.V. Knowles, T. Kim, M.S. Wong, W. Zhou, C.J. Kiely, I.E. Wachs, J. Catal., 256 (2008) 108-125.

[31] W. Ji, J. Hu, Y. Chen, Catal. Lett., 53 (1998) 15-21.

[32] R. Kourieh, V. Rakic, S. Bennici, A. Auroux, Catal. Commun., 30 (2013) 5-13.

[33] F. Di Gregorio, V. Keller, J. Catal., 225 (2004) 45-55.

[34] G. Sunita, B.M. Devassy, A. Vinu, D.P. Sawant, V.V. Balasubramanian, S.B. Halligudi, Catal. Commun., 9 (2008) 696-702.

[35] M. Kim, D. Son, J.-W. Choi, J. Jae, D.J. Suh, J.-M. Ha, K.-Y. Lee, Chem. Eng. J., 309 (2017) 187-196.

[36] M.A. Jaworski, S. Rodríguez Vega, G.J. Siri, M.L. Casella, A. Romero Salvador, A. Santos López, Appl. Catal., A, 505 (2015) 36-43.

[37] N. Shimoda, S. Umehara, M. Kasahara, T. Hongo, A. Yamazaki, S. Satokawa, Appl. Catal., A, 507 (2015) 56-64.

[38] J.S. Yoon, Y. Lee, J. Ryu, Y.-A. Kim, E.D. Park, J.-W. Choi, J.-M. Ha, D.J. Suh, H. Lee, Appl. Catal., B, 142–143 (2013) 668-676.

[39] H. Toraya, M. Yoshimura, S. Somiya, J. Am. Ceram. Soc., 67 (1984) C-119-C-121.

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Fig. 1. X-ray diffraction results of (a) ZrO<sub>2</sub> prepared in our lab, (b) 5WZr(syn), (c) 10WZr(syn),(d) 15WZr(syn), and (e) 20WZr(syn) prior to the deposition of Ru.

**Fig. 2.** Raman spectra of (a) ZrO<sub>2</sub> prepared in our lab, (b) 5WZr(syn), (c) 10WZr(syn), (d) 20WZr(syn), and (e) WO<sub>3</sub> prior to the deposition of Ru.

Fig. 3. TEM images of Ru/15WZr(syn).

**Fig. 4.** XPS spectra of (a) Ru/ZrO<sub>2</sub>(syn), (b) Ru/5WZr(syn), (c) Ru/10WZr(syn), (d) Ru/15WZr(syn), and (e) Ru/20WZr(syn).

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**Fig. 6.** Quantity of acid sites relative to the surface area and ratio of the tetragonal phase of WZr(syn) depending on the density of the tungsten surface.

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**Fig. 8.** Conversion of guaiacol and selectivity to 0-Os depending on (a) [CO]/[Ru] and (b) the quantity of acid sites, and (c) their correlation with the fraction of tungsten.

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Table 1. Catalytic results of tungstated zirconia (WZr)-supported Ru catalysts.<sup>a</sup>

Cetalant	<b>V</b> (0/)	Yield (%)				
Catalyst	$\mathbf{X}_{\mathrm{GUA}}(\%)$	0-Os	1-Os	2-Os		
Ru/15WZr(syn)	65.4	19.8	18.1	0.7		
Ru/15WZr(imp)	18.5	0.4	6.1	2.7		
Ru/15MoZr	12.8	0.1	3.2	3.8		
Ru/15VZr	26.5	0.5	12.7	2.9		

<sup>a</sup> Reaction conditions: guaiacol (8.96 mmol), catalyst (20 mg), water (29 ml), initial H<sub>2</sub> pressure at room temperature = 40 bar, 270 °C, 1 h, stirred at 800 rpm.

Support	Loading of tungsten (%) <sup>a</sup>	S <sub>BET</sub> (m²/g) <sup>b</sup>	Micropo re surface area (m²/g)	Pore width (nm)	tungsten surface density (W atom/nm <sup>2</sup> )°	Quantity of acid sites per mass (mmol/g ) <sup>d</sup>	Quantity of acid sites per surface area (µmol/m <sup>2</sup> ) <sup>e</sup>	Fraction of tetragon al ZrO <sub>2</sub> (Vt) <sup>f</sup>	[CO]/[R u] <sup>g</sup>
ZrO <sub>2</sub> (syn)	0	9.8	9.7	11.6	0.0	0.017	1.73	0	0.029
5WZr(sy n)	5.1	36.7	-	10.9	4.6	0.303	8.26	0.55	0.063
10WZr(s yn)	9.6	41.4	-	8	7.6	0.358	8.65	0.6	0.048
15WZr(s yn)	15.2	34.9	-	9.4	14.3	0.654	18.7	0.62	0.01
20WZr(s yn)	19.1	52.3	-	4.8	12.0	0.843	16.1	0.87	0.013
WO <sub>3</sub>	-	0.04	-	-	-	0.008	0.2	-	0.009

#### **Table 2.** Pore structures and metal nanoparticle properties of Ru/WZr catalysts.

<sup>a</sup>Calculated by XRF.

<sup>b</sup>BET surface area, measured by N<sub>2</sub>-physisorption.

<sup>c</sup>Surface density of tungsten, calculated by dividing the quantity of tungsten with the S<sub>BET</sub> of the catalyst [34].

<sup>d</sup>Measured by the NH<sub>3</sub>-TPD.

<sup>e</sup>Calculated using the quantity of acid sites and the BET surface area.

<sup>f</sup>Calculated from the XRD peaks by the Toraya method [39].

<sup>g</sup>Measured by the CO-chemisorption.