Effect of Cu addition as a promoter on Re/SiO₂ catalysts in the hydrodeoxygenation of 2-methoxyphenol as a model bio oil compound.

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Abstract

The promoting effect of Cu on Re/SiO₂ catalysts was studied for guaiacol hydrodeoxygenation. Cu(x)Re/SiO₂ catalysts containing from 0 to 1.91 wt% Cu and 13 wt % of Re were prepared by successive wet impregnation and characterized using X-ray diffraction (XRD), nitrogen sorption, CO chemisorption, X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and surface acidity techniques. Batch reactions were carried out at 300°C and 5 MPa of H₂. The Cu(x)Re/SiO₂ catalysts displayed higher activities than the Re/SiO₂ catalyst with a maximum activity at 1.58 wt% Cu. At loadings above 1.5 wt%, aggregate formation and a loss of metallic Re active sites lead to a decreased activity. The increase of the activity was attributed not only to Cu increasing the Re reducibility, but also to Cu somehow increasing the metallic Re active sites favoring guaiacol conversion. All catalysts displayed the same product distribution, confirming that the Cu in the Cu(x)Re/SiO₂ not change the nature of the active site in the metallic Re nanoparticles.

Keywords: Cu promoter, Re metal, hydrodeoxygenation, active sites, hydrogen spillover.

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1. Introduction

The growing demand for fossil fuels, especially oil and its derivatives, has generated the need to seek new sources to offset oil depletion. In this context, biomass has become an important source of renewable energy because significant amounts are available from the wood industry, pulp and waste paper, brewing by-products, and other forest residues.^[1]

Biomass conversion process such as gasification, direct combustion, transterification, biochemical process and pyrolysis allow biomass to be used as source of energy, chemicals and fuels. Liquid fuels can be produced at relatively high yields via fast pyrolysis (400-500 °C without O₂) which produces bio oil (60%), char (30%) and gas products (10%). It is difficult to directly use the bio-oil as a fuel because it has a large number of oxygenated compounds, has a high viscosity, is corrosive, and is thermally unstable making it unsuitable for storage and transportation. However, it has been demonstrated that hydrotreating bio-oil can produce fuels and chemicals similar to those obtained from petroleum [2, 3].

Catalytic hydrotreating is the most common process for chemical products and biofuels from bio-oil [4, 5], specifically hydrodeoxygenation (HDO), because 99% of compounds in bio oil contain oxygen. These compounds include acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, furan, phenolic lignin derivatives and terpenes [4]. Guaiacol (2-methoxyphenol) has been widely used as a model compound for HDO [6-11] because this molecule has two different organic functions (Ar-OH and Ar-OCH₃ groups), and it is considered representative of the organic phase of bio-oil.

Different active phases, such as sulfides [9, 12, 13], nitrides [14-17] and metallic catalysts [18-20] have been studied for HDO. Metallic catalysts favor hydrogenation

and oxygen removal in HDO of guaiacol [21-23], and metallic catalysts have an advantage over sulfide catalysts in that they do not require sulfur addition to the bio-oil. In fact, Gutierrez *et al.* [21] found that Pt, Pd and PtPd catalysts displayed better activity and selectivity to hydrodeoxygenated compounds than conventional CoMoS/Al₂O₃ catalyst because the sulfide catalyst was deactivated by coke deposition. Nimmanwudipong *et al.* [22] found that bifunctional Pt/ γ -Al₂O₃ catalyst in HDO of different oxygenates favored the hydrogenation/hydrogenolysis reactions along with transalkylation reactions. Supported nickel catalysts have been demonstrated to be good catalysts for HDO of anisole because of the combination of acid sites from the support, high dispersion of metallic active sites and good redox characteristics of the support [24, 25]. Furthermore, non-noble metals have been used as promoters in order to improve the catalytic activity and selectivity in HDO reactions. The addition of Co and Ni to Pt/ γ -Al₂O₃ catalyst improved *m*-cresol conversion and modified the product distribution towards the formation of more saturated cyclic hydrocarbon products by generating additional active sites for alcohol dehydration [26].

Unlike other metals, Cu has low activity for breaking C-C bonds; however, it is an efficient catalyst in hydrogenation and dehydrogenation of C-O bonds [27]. In fact, the hydrodeoxygenation of furfural on Cu/SiO₂ catalyst produces mainly furfuryl alcohol by hydrogenation of the carbonyl group [28]. The addition of Cu to Ni supported catalysts in HDO of guaiacol enhances the reduction of NiO. The acid sites generated in the catalysts favor the activation of the ArO-CH₃ bond leading to a high guaiacol conversion with the formation of deoxygenated and methylated compounds [12, 19, 29].

Rhenium-based catalysts have been widely studied as hydrotreating catalysts [9, 10, 30-37]. Rhenium sulfide catalysts have higher activities and selectivities to

hydrodeoxygenated compounds in comparison to other conventional catalysts. The higher activity of ReS_2 was attributed to a metallic-like character of the sulfide, which conferred a high ability for hydrogenation [35].

On the other hand, Leiva *et. al.* [36] studied the effect of sulfide, oxide and metallic Re supported on SiO_2 in the hydrodeoxygenation of guaiacol. The authors found that the metallic Re active phase presented the lowest activity in comparison to Re sulfide and oxide catalysts. However, the metallic Re catalysts showed a high selectivity to phenol and deoxygenated compounds, indicating that the addition of an effective promoter could improve the activity.

Considering that metallic Re is active in the hydrodeoxygenation reactions and the promising potential of Cu as promoter due to its hydrogenation/dehydration capacity [27, 38], the aim of the current work was to study promoter effects of Cu on supported Re catalysts. Guaiacol was used as model molecule for lignin-derived compounds, and Cu loadings were varied on the Re/SiO_2 catalysts in order to improve the catalytic activity.

2. Experimental

2.1 Catalyst preparation

The Cu(x)Re/SiO_2 catalysts with Cu loadings (0.32, 1.10, 1.58, 1.91 wt.%) were prepared by successive impregnation. Prior to impregnation, the SiO_2 support (SiO_2 Grace Davidson 432) was ground and sieved to obtain particle sizes between 80 and 125 μm . First, SiO_2 was impregnated by $\text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O}$ by incipient wetness. The samples were left at room temperature for 24 h and then calcined at 300 °C for 1 h. Afterwards, NH_4ReO_4 (Aldrich, 99%) as Re precursor was added by wet impregnation in aqueous solution. Around 13 wt. % of Re was used to prepare the Cu(x)Re(13)/SiO_2 catalysts. After impregnation, the samples were left at room temperature for 20 h, dried

at 110 °C for 12 h, and calcined at 300 °C for 0.5 h. Before reaction, the catalysts were reduced *ex-situ* at 400 °C for 4 h in H₂ flowing at 60 mL min⁻¹. The Cu and Re metal loading was determined by ICP using Re emission line of 221.426 nm.

2.2 Characterization of supports and catalysts

The physical properties of the catalysts and the supports are presented in Table 1. The BET specific surface area (S_{BET}) and pore volumes of the supports and catalysts were determined from nitrogen sorption measurements at -196 °C using Micromeritics TriStar II 3020 equipment. Prior to the measurements, the samples were outgassed at 300 °C for 2 h. Micropore volume (V_o) was determined by the Dubinin–Radushkevich method while the total pore volume (V_p) was recorded by nitrogen adsorption at a relative pressure of 0.99. Mesopore volume (V_m) was determined by the difference between V_p and V_o .

The total acidity of the support and the reduced catalysts were measured potentiometrically by suspending the catalysts in acetonitrile and titrating with n-butylamine using an Ag/AgCl electrode [39].

Temperature programmed reduction (TPR) was carried out in a quartz cell in a system equipped with a thermal conductivity detector. In the experiment 20 mg of the sample was heated under 5% H₂/Ar flowing at 50 mL min⁻¹. The sample was heated at 10 °C min⁻¹ from 25 °C to 1050 °C. The H₂ consumption was calculated from a calibration using solid CuO as a reference.

The CO chemisorption measurements were performed in a Micromeritics ASAP 2010 C equipment. Before analysis, the catalysts were reduced "*in situ*" for 4 h under H₂ flow at 400 °C. After reduction, the tube was evacuated at 400 °C and 35 °C to remove the remaining H₂. Finally the CO chemisorption analysis was performed at 35 °C with

pressure ranges between 0.5 to 9.5 mmHg assuming 1:1 stoichiometry of CO:Re, according to reported by J. Okal [40].

Powder x-ray diffraction (XRD) spectra were obtained using a D4 Endeavor Bruker AXS diffractometer equipped with a nickel-filtered CuK α 1 radiation (λ = 1.5418Å). Prior to analysis, the catalysts were reduced *ex-situ* in flowing H₂ (30 mL min⁻¹) at 400 °C for 4 h. Subsequently, the reactor with the catalyst was immersed for 1 h in a bath of isopropyl alcohol-liquid N₂ mixture while flowing a 5% O₂/N₂ mixture at 10 mL min⁻¹. Finally, the reactor was removed from the bath, while maintaining the O₂/N₂ flow for another hour. The standard scan parameters were 1° per minute for the 2 θ range from 10 to 90°. Identification of the phases was achieved by reference to EVA diffraction file data.

The XPS measurements were performed using a VG Escalab 200R electron spectrometer equipped with a hemispherical electron analyzer and Mg K α (1253.6 eV) X-ray source. The samples were reduced *in-situ* at 400 °C under flowing H₂ and transferred from the pretreatment chamber to the spectrometer. The intensity of the peaks was estimated by calculating the integral of each peak after subtracting an S-shaped background and fitting the experimental curve to a combination of Gaussian/Lorentzian lines. Atomic ratios were calculated by using peak areas normalized on the basis of acquisition parameters, sensitivity and transmission factors provided by the manufacturer, and determined from the corresponding peak intensities, corrected with tabulated sensitivity factors, with a precision of $\pm 7\%$.

XAS measurements were made for the Re L₃ edge (10.535 keV) and Cu K edge (8.979 keV) on the insertion devise beam line of sector 10 (MRCAT) of the Advanced Photon Source, Argonne National Laboratory. The data was collected in quick-scan, transmission mode in 2 min. The spectra were obtained at room temperature without

exposure to air in an in situ cell after reducing in 4% H₂/He at 400°C for 1h and cooled to RT. Cu foil was obtained with each Cu spectrum for energy calibration. Since a Re foil was not available for energy calibration, a W foil (L₃10.207 keV) was obtained with each Re sample. Re₂O₇, ReO₃, ReO₂, and Cu(AcAc)₂, copper(II) acetylacetonate, reference compounds were obtained from Aldrich and used to determine the shift in the XANES energy due to change in oxidation state. Phase shifts, backscattering amplitudes were obtained from reference compounds: Re₂O₇ (4 Re-O at 1.77 Å), Pt foil (12 Pt-Pt at 2.77Å for Re-Re), Cu(AcAc)₂ (4 Cu-O at 1.92 Å) and Cu foil (12 Cu-Cu at 2.66 Å). Theoretical phase and amplitude functions were also calculate from FEFF6 for Re-Cu and Cu-Re. So and $\Delta\sigma^2$ values were determined by fitting Cu and Pt foils. The XANES edge energy was determined from the inflection point of the leading edge, i.e., the maximum in the first derivative. Standard procedures using WINXAS3.1 software were used to extract the EXAFS data. The coordination parameters were obtained by a least square fit in k- and r-space of the isolated multiple-shell, k²-weighted Fourier transform data.

2.3. Catalytic reaction tests

Hydrodeoxygenation of guaiacol was carried out in an autoclave batch reactor. The liquid reactant feed, consisting of guaiacol (0.232 mol L⁻¹) in n-dodecane (80 mL) with hexadecane (0.0341 mol L⁻¹) as an internal standard, was introduced into the reactor. Then, approximately 0.200 g of freshly reduced catalyst was added. The system was closed, and to avoid any air contamination, N₂ was bubbled through the solution for 10 min. Still under N₂, the reactor was heated to the reaction temperature of 300 °C while stirring. When the reaction temperature was reached, the reactor pressure was 0.5 MPa, and then H₂ was introduced into the reactor increasing the pressure to 5 MPa which was kept constant during the course of the experiment. Condensed samples were

periodically collected during the reaction and were analyzed for species identification using a Perkin Elmer Clarus 680 gas chromatograph coupled to a GCMS-SQ8T mass spectrometer. The samples were quantified using a Perkin Elmer (Clarus 400) gas chromatograph equipped with a flame ionization detector and a CP-Sil 5 column (Agilent, 30 m × 0.53 mm × 1.0 μm film thickness). The specific rate for the total conversion of guaiacol was calculated from the initial slope of the conversion vs. reaction time plot. The intrinsic rate was calculated from the specific rate according to the following equation:

$$r_I = r_s \frac{N}{n\text{Re}} \quad (1)$$

Where r_I is the intrinsic rate (molecules of guaiacol transformed per Re atom per second), r_s is the specific rate (moles of guaiacol transformed per gram of catalyst per second), $n\text{Re}$ represents the total number of Re atoms per gram of catalyst, and N is Avogadro's number. The intrinsic and specific deoxygenation (HDO) rate was calculated for the conversion of guaiacol to O-free compounds (benzene, cyclohexane, cyclohexene and methylated analogs). Selectivities (%) were determined at 20% guaiacol conversion. The carbon balance accounting for the HDO reactions was approximately 95%. The experiments were carried out two times and the results agreed within 5%.

3. Results and discussion

3.1 Catalysts and support Characterization

The textural properties of the SiO_2 support, Re/SiO_2 and Cu(x)Re/SiO_2 catalysts which were obtained from nitrogen sorption isotherms are presented in Table 1. The pore volume decreases only about 13 % after Re deposition suggesting that there was no significant pore mouth blockage. The promoted Cu(x)Re/SiO_2 catalysts present similar

textural properties to the non-promoted catalysts, indicating that the small quantities of Cu do not significantly affect the specific surface area and pore volumes of the catalysts.

The results of initial electrode potential (E_0) of the SiO_2 support, Re/SiO_2 and Cu(x)Re/SiO_2 reduced catalysts are also presented in Table 1. The Re/SiO_2 and Cu(0.32)Re/SiO_2 catalysts had similar initial electrode potential, while the other catalysts and the support have lower values. The acid strength can be determined according to the criterion proposed by Cid and Pecchi [39]: $E_0 > 100$ mV, very strong acid sites; $0 < E_0 < 100$ mV, strong acid sites; $-100 < E_0 < 0$ mV, weak acid sites; $E_0 < -100$ mV, very weak acid sites. The results indicate that the Cu(1.58)Re/SiO_2 catalyst has very weak acid sites, while the other catalysts and SiO_2 support have weak acid sites. The increased acid strength in Re/SiO_2 catalyst relative to SiO_2 support can be due to formation of Lewis acid sites attributed to presence of ReO_x type species, in agreement to a previous finding reported by Lan *et al.* [41]. This oxide remaining after reduction is consistent with the XPS results (see below). On the other hand, the acid strength decreased gradually with the increase of Cu content up to 1.58 wt%, then increased. The decrease of acid strength can be attributed to that Cu slightly favors the reduction of Re oxide species decreasing the Lewis acid sites on Re surface [41]. Over 1.58 wt% Cu, a slight increase in acid strength in the weak acid sites range was observed in the Cu(1.58)Re/SiO_2 catalyst. This result can be attributed to the formation of small CuRe aggregates (suggested by XPS results), which allows Si-OH bond characteristics of the SiO_2 to reappear on the surface, increasing the acid strength.

Figure 1 presents the X-ray diffraction (XRD) patterns of passivated Re/SiO_2 and Cu(x)Re/SiO_2 catalysts. The $\text{ReO}_x/\text{SiO}_2$ and Cu(2%)/SiO_2 catalysts are shown as references in Fig. 1. The Re/SiO_2 catalyst has diffraction peaks at $2\theta = 37.5^\circ$, 40.4° ,

42.7°, 56.4°, 67.6°, 75.0°, 80.9° and 83.4°, which can be attributed to metallic Re [42]. The Cu(2%)/SiO₂ catalyst has diffraction peaks at $2\theta = 43.3^\circ$, 50.5° and 74.1° which can be attributed to metallic Cu [42]. ReO_x/SiO₂ catalyst shows diffraction peaks at $2\theta = 16.6^\circ$, 25.5° , 27.4° , 30.4° , 39.9° , 43.0° , 47.4° , 49.1° , 50.7° , 56.8° , 60.7° , 66.0° and 69.6° assigned to ReO₄⁻ species [42] and at $2\theta = 34.6^\circ$ and 37.9° assigned to ReO₃ [42], indicating that ReO₄⁻ is the main species in the Re oxide catalysts. The most intense diffraction peak of metallic Cu at 43.4° , assigned to (111) *hkl* plane of a face-centered cubic geometry, is very close to the (101) *hkl* plane of Re metal with hexagonal geometry. Note that the Cu(x)Re/SiO₂ diffraction patterns are similar to the Re/SiO₂ catalyst, and there is little evidence for metallic Cu. Table 2 summarizes the three most intense diffraction planes of Re based catalysts ($2\theta_1$, $2\theta_2$, $2\theta_3$) and cell parameters (“a” and “c”) of a hexagonal geometry assigned to Re metal. Table 2 shows that the cell parameters of Re do not change significantly with increasing Cu content, suggesting that this metal does not modify the hexagonal structure of Re. However, due to a higher Re/Cu atomic ratio obtained by XPS (shown later) one cannot rule out that nanoparticles of Cu, not detected by XRD, are inserted into crystalline structure of Re.

Table 3 presents the CO chemisorption results for the Re/SiO₂ and Cu(x)Re/SiO₂ catalysts. In this table, the particle diameter increases, while the metallic surface area and apparent dispersion slightly decrease with Cu content, suggesting that Cu disfavors Re dispersion. Wagner *et al.* [43] showed that Cu has a high affinity to the metallic Re surface, indicating that Cu may have migrated onto and/or close the surface of Re particles during the reduction step. Considering the similar behavior of Ru and Re species as active phases, the CO chemisorption result can be correlated to the observed previously by Salazar *et al.* [44] on CuRu catalysts. Where, the Cu onto/close the surface of Re could be in monolayer or bilayer coverage (depending on the Re content),

lead to a decrease of CO chemisorption capacity on Re surface and therefore an apparent decrease of dispersion. On the other hand, decreasing Re dispersion with increasing Cu content suggests a weak interaction of Re with the support. This behavior can be expected since Cu precursors were impregnated first, occupying the support adsorption sites disfavoring the dispersion of Re. The decreasing Re dispersion was intensified when the Cu content was increased, leading to formation of Re aggregates, in agreement with acid strength measurements.

The catalysts were also analyzed by TEM to obtain the particles size distribution. However, it was not possible distinguish between Cu and Re particles in the TEM micrographs shown in supplementary material (Fig S1).

Figure 2 presents the TPR profiles of $\text{ReO}_x/\text{SiO}_2$ and $\text{Cu}(x)\text{ReO}_x/\text{SiO}_2$ precursors. The $\text{ReO}_x/\text{SiO}_2$ precursor displayed a peak at 331 °C, which was assigned to reduction of ReO_3 to Re^0 and another peak at 357 °C attributed to the reduction of Re_2O_7 to Re^0 based on the previously reported work by Arnoldy *et. al.* [45]. This result suggests that the main species formed during the decomposition of the NH_4ReO_4 precursor during the calcination step is ReO_3 . However, the XRD of $\text{ReO}_x/\text{SiO}_2$ catalyst (Fig. 1) shows that $\text{ReO}_4^- (\text{Re}^{7+})$ is the principal specie present on SiO_2 . This result indicates that ReO_4^- is the main species remaining after calcination step, and therefore the principal peak at 331 °C can be attributed to the reduction of Re^{7+} to Re^0 , and the minor contribution at 357 °C can be to reduction from Re^{6+} to Re^0 . However, the calculated H_2 consumption shows that the reducibility of ReO_x on $\text{ReO}_x/\text{SiO}_2$ and $\text{Cu}(x)\text{ReO}_x/\text{SiO}_2$ catalysts were around 70 % and 90% respectively in agreement to XPS results. These results suggest that the Cu improves the reduction of Re.

The TPR profiles of the $\text{Cu}(x)\text{ReO}_x/\text{SiO}_2$ catalysts were all similarly shaped (up to 1.58 wt.% Cu), but with a shift to lower temperature. This behavior was attributed to

a hydrogen spillover mechanism [19, 46] which can be originated from two effects; the Cu slightly promotes Re reduction and/or, the presence of Re^0 generates an autocatalysis mechanism [45].

The catalyst with 1.91 wt% Cu shows only a single reduction peak, due to the high Re/Cu molar ratio around of 2 can lead to overlap of reduction peak of Cu and Re precursors. The results of TPR obtained suggest that the Cu may change the $\text{ReO}_3/\text{Re}_2\text{O}_7$ ratio on the support leading to a width peak of Re reduction. Furthermore, the possibility that, at higher loading, Cu influences the Re dispersion cannot be discounted.

Figure 3 shows the XP spectra of Re/SiO_2 and $\text{Cu}(0.32)\text{Re}/\text{SiO}_2$ reduced catalysts. Fig. 3a and 3b show that Re presents two partially overlapping doublets, each one containing the $\text{Re } 4f_{7/2}$ and $\text{Re } 4f_{5/2}$ peaks, indicating the presence of two phases. Only one doublet is observed for the $\text{Cu } 2p_{3/2}$ peak, indicating the presence of only one phase; similar results were observed for the other catalysts (not shown).

Table 4 summarizes the binding energies (BE) of the most intense $\text{Re } 4f_{7/2}$ and $\text{Cu } 2p_{3/2}$ components of each doublet, its relative proportion (in parentheses) and the surface atomic ratio for all promoted catalysts along with the unpromoted Re/SiO_2 catalyst. This table shows that the Re has two binding energies, the main contribution at 40.7 eV associated with a Re^0 species [47, 48], and a minor contribution at 42.1 eV assigned to a Re^{4+} species [49]. Note that the percentage of the metallic Re phase increases with the Cu content (up to 1.58 wt% Cu), suggesting that the Cu promotes the reduction of ReO_x species, which is consistent with the TPR profiles. In addition, Table 4 shows a single contribution of Cu at 931.7 eV of binding energy in all bimetallic catalysts, this was assigned to Cu^0 species [50].

Table 4 and Fig. 4 show that the Re/Si surface atomic ratio slightly decreases with Cu content up to 1.58 wt.% of Cu. Then, a marked decrease in Re/Si surface atomic ratio is observed with 1.91 wt.% Cu. The decrease in the Re/Si surface atomic ratio with increasing Cu content could be attributed to this metal cover mainly the surface SiO₂ support disfavoring the Re-support interaction, leading to decrease of Re dispersion, in agreement to CO chemisorption results. This behavior is more pronounced in the catalyst with the highest Cu content. However, cannot be ruled out that the migration of Cu over the Re particles leads to a smaller quantity of Re exposed on the surface and thus to a decreased Re/Si atomic ratio. Table 4 and Fig. 4 show the values of Cu/Si atomic ratio for Cu(x)Re/SiO₂ catalysts. Figure 4 shows a relatively linear increase in the Cu/Si atomic ratio up to 1.58 wt. % of Cu, suggesting a homogeneous dispersion of Cu on the catalyst surface. However, at 1.91 wt% Cu, the Cu/Si atomic ratio increased more dramatically. This increase suggests the formation of larger particles of Cu on the support. This higher value is in agreement with the decrease of the Re/Si atomic ratio at 1.91 wt% Cu.

The EXAFS are shown in the Supplementary Material (Fig. S1 to Fig S6) and the results are summarized in the Table 5 for the Cu(1.58)Re/SiO₂ catalyst. The results are presented according to Cu-O, Re-O, Cu-Cu, Re-Re binding, before and after H₂ treatment, and correlated to patterns for Re/SiO₂ and the ReCu(1.58)/SiO₂ catalysts. Table 5 shows that, before reduction, in the Cu edge the energy of the pre-edge in the XANES is consistent with Cu²⁺ species and the EXAFS give 4 Cu-O bonds at 1.92 Å. In case of the Re edge, the energy of the XANES is consistent with Re⁷⁺ species, and the EXAFS gives 4 Re-O at 2.77 Å, indicating the formation of Re₂O₇.

After H₂ treatment at 400 °C, the EXAFS indicates the only presence of pure metallic Cu with the coordination number is near 6.1 (bulk foil = 12) at a normal Cu-Cu

distance of 2.55 Å. A coordination of 6.1 is consistent with nano-particles of about 1.5-2.5 nm in size. At the Re edge, the EXAFS indicates that Re is reduced to metallic nanoparticles (NP's), where the coordination shows only Re-Re bonds (coordination number of 9.5 at 2.73 Å), and consistent with independent Re NP's of about 5 nm. The EXAFS results indicate that the fit is not improved by inclusion of Cu-Re, indicating little Re in the Cu nanoparticles. Also, the fit is not improved by inclusion of a Re-Cu scatter, and the EXAFS matches that of Re NP's (no possibility of Cu) prepared in other studies. Thus, there is little Cu, if any, associated with the Re nanoparticles, rather it appears this sample has small Cu nanoparticles and independent, larger Re nanoparticles. While it would be difficult to detect a small amount of CuRe interaction at the Re edge due to the high loading of Re in the sample, at the Cu edge, if CuRe interactions would be observed if they occurred. The metallic Cu in the CuRe/SiO₂ is identical to that on Cu/SiO₂ suggesting that these two metals do not form a bimetallic nanoparticle.

3.2 Catalytic activity of Cu(x)Re/SiO₂ catalysts

Fig. 5 presents the conversion of guaiacol and yield of products as function of reaction time on the Re/SiO₂ and Cu(x)Re/SiO₂ catalysts. The main reaction products on the Cu(x)Re/SiO₂ catalysts were phenol, cyclohexane, anisole, cyclohexane and BTX type compounds (benzene, toluene and xylene). Meanwhile, the Re/SiO₂ catalyst produced primarily phenol and methanol. For the catalyst with 1.58 wt% Cu, the phenol and cyclohexane compounds increase with time up to a maximum and then decrease. This trend suggests that phenol and cyclohexane are reaction intermediates. Furthermore, cyclohexanone, methanol, cyclohexane and methylcyclohexane compounds were observed as minor products in all the systems studied.

The transformation pathways of guaiacol on the Cu(x)Re/SiO₂ catalysts are consistent with those previously reported by Leiva *et al.* [36] for Re metallic catalyst. Fig. 6 shows that on all catalysts studied, the main transformation route is the demethoxylation (DMO) of guaiacol to form phenol. X. Zhang *et al.* [51] suggests that the phenol and methanol are formed after a homolytic dissociation of the activated C_{Ar}-OCH₃ and consequently hydrogenation of radicals under H₂ pressure. Then the subsequent direct deoxygenation (DDO) of phenol and hydrogenation steps leading to the formation of cyclohexane and BTX compounds. The formation of xylene was by methylation (ME) pathway. Moreover, the promoted catalysts present a larger amount of anisole at 4 h of reaction, formed by direct deoxygenation of guaiacol (DDO). The DDO reaction occurs in parallel to the DMO route forming deoxygenated products.

Table 6 summarizes the initial specific rate (r_s), the initial intrinsic rate (r_I) of guaiacol transformation and the HDO rate (r_{HDO}) on Re/SiO₂, Cu(x)Re/SiO₂ and Cu/SiO₂ catalysts. The Table shows that the Cu(x)Re/SiO₂ catalysts displayed a higher intrinsic rate than the Re/SiO₂ catalyst in all the Cu contents studied with a maximum activity at 1.58 wt% of Cu. A similar trend was observed for r_{HDO} . This behavior is more clearly presented in Fig.7. Table 6 also shows that there is almost no activity on the reference Cu(2%)/SiO₂ catalyst. Therefore, these results suggest that the increase observed in the activity must be attributed to a promoter effect of Cu on Re catalysts. The TPR, XPS and X-ray absorption (XANES and EXAFS) results show the presence of higher proportion of Re⁰ with Cu addition, suggesting that the promoter effect of copper can be due to its ability to increase (or “promote”) the reducibility of ReOx species. However, the activity increased as much as 16 times, while the reducibility increased only 1.13 times, suggesting that the increase in activity is not explained solely

by increased reducibility or that there is a non-linear relationship between reducibility and activity.

The increase in the activity also could be attributed to an effect of Cu on Re particle size, similar to observed by Kang *et al.* [52], however the TEM was not effective to obtain the estimation of Re particles size. Also, the Cu promoter effect observed could be due to the formation of hydrogen spillover (H_{SO}) on metallic Cu improving the catalytic activity of Re metal [53-55]. Other possibilities are that there is a Cu-Re electronic effect or that Cu acts as a receiver to collect hydrogen or other reaction intermediates activated on Re active sites, similar to what has been observed previously in NiCu catalysts [56]. This synergism has not been observed previously and it need additional experiment to find the real effect of Cu on Re active site.

The decrease of catalytic activity of Cu(1.91)Re/SiO₂ catalyst was attributed to the loss of active sites by more remarkable formation of aggregates of CuRe, as was suggested by XPS and CO chemisorption.

Fig. 8 shows of the distributions of products calculated at a guaiacol conversion of 20% over all catalysts. The distribution of products is not significantly modified by the Cu addition, indicating that the Cu metal only increase the number of active sites without changing their nature. Bui. *et al.* [12] showed that the transformation route (DME and DMO) are directly related to acid strength of catalysts; strong acid sites leading DME route, while weak acid sites promotes the DMO route. In fact, Leiva *et al.* [36] later demonstred that MoP(x)/ γ -Al₂O₃ catalysts with different acid strength, but all $E_0 < 0$ mV does not affect the distribution of products in guaiacol conversion. Furthermore, differences in acid strength observed on the promoted catalysts do not affect the distribution of products.

4. Conclusions

This study showed that the addition of Cu had a positive effect on the catalytic activity of metallic Re catalysts on the guaiacol hydrodeoxygenation. The decrease in the XPS Re/Si atomic ratio was related to lower Re-support interaction influence by the presence of Cu, which also could favor the reduction of the catalyst, which is supported by TPR, acid strength techniques, and EXAFS measurements. Therefore, the increase in the catalytic activity and the greater yield of deoxygenated compounds on Cu(x)Re/SiO₂ catalysts, up to 1.58 wt.% of Cu content, can be attributed to different effects and additional experiments need to be conducted to clarify this effect. The decrease of catalytic activity over 1.58wt.% of Cu content was due to the loss of active sites by more remarkable formation of aggregates of CuRe, such was suggested by XPS and CO chemisorption. On the other hand, the selectivity on Re/SiO₂ catalyst was not modified by Cu addition, indicating that the Cu effectively increases the formation of metallic Re active sites without changing the nature of the active sites.

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References

- [1] J.D. Adjaye, N.N. Bakhshi, *Fuel Process. Technol.* 45 (1995) 185-202.
- [2] X. Zhang, T. Wang, L. Ma, Q. Zhang, X. Huang, Y. Yu, *Appl. Energy* 112 (2013) 533-538.
- [3] Q. Bu, H. Lei, A.H. Zacher, L. Wang, S. Ren, J. Liang, Y. Wei, Y. Liu, J. Tang, Q. Zhang, R. Ruan, *Bioresour. Technol.* 124 (2012) 470-477.
- [4] Q. Zhang, J. Chang, T. Wang, Y. Xu, *Energy. Convers. Manage.* 48 (2007) 87-92.
- [5] A.V. Bridgwater, S. Czernik, J. Piskorz, in: A.V. Bridgwater (Ed.), *Fast pyrolysis of biomass: A handbook*, Antony Rowe Ltd., Chippenham, UK, 2002, pp. 1-22.
- [6] E. Laurent, B. Delmon, *Appl. Catal., A* 109 (1994) 97-115.
- [7] P. Grange, E. Laurent, R. Maggi, A. Centeno, B. Delmon, *Catal. Today* 29 (1996) 297-301.
- [8] E. Furimsky, *Catalysis Reviews* 25 (1983) 421-458.
- [9] C. Sepúlveda, R. García, P. Reyes, I.T. Ghampson, J.L.G. Fierro, D. Laurenti, M. Vrinat, N. Escalona, *Appl. Catal., A* 475 (2014) 427-437.
- [10] K. Leiva, C. Sepúlveda, R. García, J.L.G. Fierro, N. Escalona, *Catal. Commun.* 53 (2014) 33-37.
- [11] K. Leiva, C. Sepulveda, R. Garcia, J.L.G. Fierro, P. Reyes, I.T. Ghampson, P. Baeza, M. Villarroel, N. Escalon, *J. Chil. Chem. Soc.* 58 (2013) 1947-1951.
- [12] V.N. Bui, D. Laurenti, P. Afanasiev, C. Geantet, *Appl. Catal., B* 101 (2011) 239-245.
- [13] M. Ferrari, R. Maggi, B. Delmon, P. Grange, *J. Catal.* 198 (2001) 47-55.
- [14] C. Sepúlveda, K. Leiva, R. García, L.R. Radovic, I.T. Ghampson, W.J. DeSisto, J.L.G. Fierro, N. Escalona, *Catal. Today* 172 (2011) 232-239.
- [15] I.T. Ghampson, C. Sepulveda, R. Garcia, B.G. Frederick, M.C. Wheeler, N. Escalona, W.J. DeSisto, *Appl. Catal., A* 413-414 (2012) 78-84.
- [16] I.T. Ghampson, C. Sepulveda, R. Garcia, J.L. Garcia Fierro, N. Escalona, W.J. DeSisto, *Appl. Catal., A* 435-436 (2012) 51-60.
- [17] I.T. Ghampson, C. Sepulveda, R. Garcia, L.R. Radovic, J.L.G. Fierro, W.J. DeSisto, N. Escalona, *Appl. Catal., A* 439-440 (2012) 111-124.

- [18] R.N. Olcese, M. Bettahar, D. Petitjean, B. Malaman, F. Giovanella, A. Dufour, *Appl. Catal., B* 115–116 (2012) 63-73.
- [19] X. Zhang, T. Wang, L. Ma, Q. Zhang, Y. Yu, Q. Liu, *Catal. Commun.* 33 (2013) 15-19.
- [20] B. Güvenatam, O. Kurşun, E.H.J. Heeres, E.A. Pidko, E.J.M. Hensen, *Catal. Today* 233 (2014) 83-91.
- [21] A. Gutierrez, R.K. Kaila, M.L. Honkela, R. Slioor, A.O.I. Krause, *Catal. Today* 147 (2009) 239-246.
- [22] R.C. Runnebaum, T. Nimmanwudipong, D.E. Block, B.C. Gates, *Catalysis Science & Technology* 2 (2012) 113-118.
- [23] M.A.n. González-Borja, D.E. Resasco, *Energy Fuels* 25 (2011) 4155-4162.
- [24] Y. Yang, C. Ochoa-Hernández, V.A. de la Peña O'Shea, P. Pizarro, J.M. Coronado, D.P. Serrano, *Appl. Catal., B* 145 (2014) 91-100.
- [25] S. Jin, Z. Xiao, C. Li, X. Chen, L. Wang, J. Xing, W. Li, C. Liang, *Catal. Today* 234 (2014) 125-132.
- [26] P.T.M. Do, A.J. Foster, J. Chen, R.F. Lobo, *Green Chem.* 14 (2012) 1388-1397.
- [27] J. Runeberg, A. Baiker, J. Kijenski, *Appl. Catal.* 17 (1985) 309-319.
- [28] S. Sitthisa, D.E. Resasco, *Catal. Lett.* 141 (2011) 784-791.
- [29] A. Popov, E. Kondratieva, J.M. Goupil, L. Mariey, P. Bazin, J.-P. Gilson, A. Travert, F. Maugèr, *J. Phys Chem. C* 114 (2010) 15661-15670.
- [30] N. Escalona, M. Vrinat, D. Laurenti, F.J. Gil Llabrás, *Appl. Catal., A* 322 (2007) 113-120.
- [31] P.E. Ruiz, K. Leiva, R. Garcia, P. Reyes, J.L.G. Fierro, N. Escalona, *Appl. Catal., A* 384 (2010) 78-83.
- [32] C. Sepulveda, N. Escalona, R. Garcia, D. Laurenti, M. Vrinat, *Catal. Today* 195 (2012) 101-105.
- [33] G. Lagos, R. García, A.L. Agudo, M. Yates, J.L.G. Fierro, F.J. Gil-Llabrás, N. Escalona, *Appl. Catal., A* 358 (2009) 26-31.
- [34] C. Sepulveda, V. Bellière, D. Laurenti, N. Escalona, R. García, C. Geantet, M. Vrinat, *Appl. Catal., A* 393 (2011) 288-293.
- [35] C. Sepulveda, R. Garcia, N. Escalona, D. Laurenti, L. Massin, M. Vrinat, *Catal. Lett.* 141 (2011) 987-995.

- [36] K. Leiva, N. Martinez, C. Sepulveda, R. García, C.A. Jiménez, D. Laurenti, M. Vrinat, C. Geantet, J.L.G. Fierro, I.T. Ghampson, N. Escalona, *Appl. Catal., A* 490 (2015) 71-79.
- [37] K. Leiva, C. Sepúlveda, R. García, J.L.G. Fierro, G. Aguila, P. Baeza, M. Villarroel, N. Escalona, *Appl. Catal., A* 467 (2013) 568-574.
- [38] C. Montassier, J.C. Menezo, J. Moukolo, J. Naja, J. Barbier, J.P. Boitiaux, in: J.B.C.B.D.D.G.P.R.M. M. Guisnet, C. Montassier (Eds.), *Stud. Surf. Sci. Catal.*, Elsevier, 1991, pp. 223-230.
- [39] R. Cid, G. Pecchi, *Appl. Catal.* 14 (1985) 15-21.
- [40] J. Okal, *Appl. Catal., A* 287 (2005) 214-220.
- [41] L. Ma, Y. Li, D. He, *Chinese Journal of Catalysis* 32 (2011) 872-876.
- [42] R.W.G. Wyckoff, *Crystal Structures - Volume 1*, Interscience Publishers, New York, 1963.
- [43] R. Wagner, D. Schlatterbeck, K. Christmann, *Surf. Sci.* 440 (1999) 231-251.
- [44] J.B. Salazar, D.D. Falcone, H.N. Pham, A.K. Datye, F.B. Passos, R.J. Davis, *Appl. Catal., A* 482 (2014) 137-144.
- [45] P. Arnoldy, E.M. van Oers, O.S.L. Bruinsma, V.H.J. de Beer, J.A. Moulijn, *J. Catal.* 93 (1985) 231-245.
- [46] M. Villarroel, E. Camú, N. Escalona, P. Ávila, S.B. Rasmussen, P. Baeza, F. Gil-Llambías, *Appl. Catal., A* 399 (2011) 63-68.
- [47] J. Okal, W. Tylus, L. Kepinski, *J. Catal.* 225 (2004) 498-509.
- [48] A. Naor, N. Eliaz, L. Burstein, E. Gileadi, *Electrochemical and Solid State Letters* 13 (2010) D91-D93.
- [49] W.T. Tysoe, F. Zaera, G.A. Somorjai, *Surf. Sci.* 200 (1988) 1-14.
- [50] G.D. Khattak, A. Mekki, M.A. Gondal, *Appl. Surf. Sci.* 256 (2010) 3630-3635.
- [51] X. Zhang, Q. Zhang, T. Wang, L. Ma, Y. Yu, L. Chen, *Bioresource Technology* 134 (2013) 73-80.
- [52] K.H. Kang, U.G. Hong, J.O. Jun, J.H. Song, Y. Bang, J.H. Choi, S.J. Han, I.K. Song, *J. Mol. Catal. A: Chem.* 395 (2014) 234-242.
- [53] C. Navarrete, R. García, C. Sepulveda, F.J. Gil-Llambias, J.L.G. Fierro, N. Escalona, *Catal. Lett.* 141 (2011) 1796-1802.
- [54] B. Delmon, *Bull. Soc. Chim. Belg.* 88 (1979) 979-987.
- [55] B. Delmon, G.F. Froment, *Catal. Rev. - Sci. Eng.* 38 (1996) 69-100.
- [56] Y. Yao, D.W. Goodman, *J. Mol. Catal. A: Chem.* 383-384 (2014) 239-242.

Table 1: Physical characteristics and acid strength of the support and catalysts

Samples	Re wt% ^a	Cu wt% ^a	S _{BET} (m ² g ⁻¹)	V _p (cm ³ g ⁻¹) ^b	V _o (cm ³ g ⁻¹) ^c	V _m (cm ³ g ⁻¹) ^d	Acid strength E ₀ (mV) ^e
SiO ₂	--	--	301	1.12	0.15	0.97	-50
ReO _x /SiO ₂	12.9	--	286	0.97	0.13	0.84	-10
CuReO _x /SiO ₂	11.5	0.32	230	0.88	0.12	0.76	-5
CuReO _x /SiO ₂	12.3	1.10	223	0.81	0.11	0.70	-82
CuReO _x /SiO ₂	13.7	1.58	220	0.88	0.11	0.77	-109
CuReO _x /SiO ₂	11.5	1.91	215	0.80	0.11	0.69	-76

^ameasured by ICP ^bV_p= total volume, ^cV_o = micropore volume. ^dV_m = mesopore volume
^eTotal acidity determined for reduced catalysts.

Table 2: Crystalline parameters obtained from X-ray diffraction patterns of Re and Cu(x)Re supported catalysts

Catalysts	$2\theta_1$ (1,0,1)	$d_{(1,0,1)}$ Å	$2\theta_2$ (0,0,2)	$d_{(0,0,2)}$ Å	$2\theta_3$ (1,0,0)	$d_{(1,0,0)}$ Å	a^* Å	c^* Å
Re/SiO₂	42.7	2.11	40.4	2.23	37.5	2.39	2.76	4.46
Cu(0.32)Re/SiO₂	42.9	2.11	40.6	2.22	37.6	2.39	2.77	4.44
Cu(1.10)Re/SiO₂	43.0	2.10	40.7	2.21	37.8	2.38	2.75	4.42
Cu(1.58)Re/SiO₂	43.1	2.10	40.8	2.21	37.9	2.37	2.75	4.42
Cu(1.91)Re/SiO₂	43.0	2.10	40.7	2.21	37.7	2.38	2.75	4.42

*a y c cell parameters of metallic Re with a hexagonal geometry (P6-3/m)

Table 3: Particle diameter, metallic surface area and dispersion determined from CO chemisorption measurements of Re and Cu(x)Re supported catalysts

Catalysts	Particle diameter (nm)	Metallic surface area (m² g⁻¹)	Apparent dispersion (%)
Re/SiO₂	7	29	11
Cu(0.32)Re/SiO₂	13	18	9.4
Cu(1.10)Re/SiO₂	19	12	6.5
Cu(1.58)Re/SiO₂	19	12	6.5
Cu(1.91)Re/SiO₂	21	11	7.2

Table 4: XPS binding energies (eV) and surface atomic ratio of Re and Cu(x)Re supported reduced catalysts.

Catalysts	Re4f _{7/2} (eV)	Cu2p _{3/2} (eV)	Re/Si at	Cu/Si at
Re/SiO ₂	40.3 (78) 42.4 (22)	---	0.065	---
Cu(0.32)Re/SiO ₂	40.7 (83) 42.1 (17)	931.7	0.059	0.0020
Cu(1.10)Re/SiO ₂	40.6 (85) 42.2 (15)	931.7	0.056	0.0046
Cu(1.58)Re/SiO ₂	40.6 (88) 42.2 (12)	931.7	0.058	0.0061
Cu(1.91)Re/SiO ₂	40.7 (84) 42.2 (16)	931.7	0.049	0.0092

Table 5: X-ray absorption (XANES and EXAFS) measurements for Re L₃ edge and Cu K edge of Re/SiO₂ and Cu(1.58)Re/SiO₂ catalysts.

Sample	Treatment	Edge Energy, keV	Scatter	N	R, Å	$\Delta\sigma^2$ (x 10 ³)	Eo, eV	Comment
References								
Re Foil	Standard	10.5350	Re-Re	12	2.75			
ReO₂	Standard	10.5386						
ReO₃	Standard	10.5395						
Re₂O₇	Standard	10.5343	Re-O	4	1.74			
Cu Foil	Standard	8.9790	Cu-Cu	12	2.56			
Cu(AcAc)₂	Standard	8.9978 Pre-edge	Cu-O	4	1.92			Cu(II)
Cu Edge								
	Air	8.9781 Pre-edge	Cu-O	4.0	1.96	1.0	-4.4	Cu(II)
CuRe/SiO₂	H ₂ 400°C	8.9792	Cu-Cu	6.1	2.55	3.0	-1.5	Cu(0)
Re Edge								
	Air	10.5346	Re-O	4.2	1.77	0.0	-0.1	Re(VII)
ReCu/SiO₂	H ₂ 400°C	10.5330	Re-Re	9.5	2.73	1.0	-3.0	Re(0)

Table 6: Catalytic activity of the Cu(x)Re/SiO₂ catalysts

Catalysts	$r_S \cdot 10^5$ (mol g _{cat} ⁻¹ s ⁻¹)	$r_{HDO} \cdot 10^3$ (molec. Re at. ⁻¹ s ⁻¹)	$r_I \cdot 10^3$ (molec. Re at. ⁻¹ s ⁻¹)
Re/SiO ₂	0.1	0.30	1.4
*Cu(2)/SiO ₂	0.02	---	---
Cu(0.32) Re/SiO ₂	0.99	4.57	15
Cu(1.10) Re/SiO ₂	1.11	3.36	17
Cu(1.58) Re/SiO ₂	1.80	7.20	25
Cu(1.91) Re/SiO ₂	1.01	3.17	16

*Included as reference

Figure Captions

Figure 1: X-ray diffraction patterns of $\text{ReO}_x/\text{SiO}_2$, $\text{Cu}(2\%)/\text{SiO}_2$ and $\text{Cu}(x)\text{Re}/\text{SiO}_2$ catalysts

Figure 2: Temperature programmed reduction (TPR) of $\text{Cu}(x)\text{Re}/\text{SiO}_2$ catalysts

Figure 3: XP spectra of a) $\text{Re}4f$ in Re/SiO_2 b) $\text{Re}4f$ in $\text{Cu}(0.32)\text{Re}/\text{SiO}_2$ and c) $\text{Cu}2p$ in $\text{Cu}(0.32)\text{Re}/\text{SiO}_2$ catalysts.

Figure 4: Calculated and measured XPS Re/Si and Cu/Si atomic ratios as a function of Cu content.

Figure 5: Variation of the transformation of guaiacol and the yield of products with time for a) Re/SiO_2 , b) $\text{Cu}(0.32)\text{Re}/\text{SiO}_2$, c) $\text{Cu}(1.10)\text{Re}/\text{SiO}_2$, d) $\text{Cu}(1.58)\text{Re}/\text{SiO}_2$ and e) $\text{Cu}(1.91)\text{Re}/\text{SiO}_2$ catalysts.

Figure 6: Reaction network for the conversion of guaiacol over Re/SiO_2 catalyst [36]

Figure 7: Comparison of intrinsic rate and HDO rate as function of Cu content.

Figure 8: Selectivity at 20% conversion of guaiacol on $\text{Cu}(x)\text{Re}/\text{SiO}_2$ catalysts.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8