Cu/KIT-5 catalysts for hydrogenation of fatty acids: a comprehensive study of the chemical species and their performance

Diego Valencia¹ · Diana Gómora-Herrera¹ · Rosa Isela Conde¹ · Perla Morales-Gil¹ · Jorge Aburto¹

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Abstract

Cu as an active phase represents a great alternative in heterogeneous catalysis for biomass feedstocks. New Cu/KIT-5 catalysts were synthesized by varying the metal precursor in aqueous solution. Copper chloride, nitrate or sulfate were impregnated to three-dimensional mesoporous KIT-5 material and the catalysts were characterized. The catalysts were tested in hydrogenation of palmitic acid. We found that the catalytic activity trend as a function of the salt precursor is: $\text{NO}_3^- > \text{Cl}^- = \text{SO}_4^{2-}$. The catalyst prepared with CuSO_4 resulted in high quantities of linear alkanes and alkenes, while the other two materials prefer the hydrogenation reaction to the alcohol. The hydrocarbon molecules produced over these Cu/KIT-5 materials point out the possibility of tuning their selectivity to desired products. Those features might be exploited for cleaner catalysts applied to biomass transformation.

Keywords Copper · Hydrogenation · KIT-5 · Biomass

1 Introduction

Depletion of fossil reservoirs and global warming are key elements for the development of sustainable processes and new energy carriers. Linear hydrocarbons such as alkanes are important class of molecules with a variety of chemical applications [1]. Processing of vegetable oils, composed by triacylglycerides and fatty acids, is an alternative to provide these hydrocarbons from renewable resources. The chemical composition of this biomass feedstock requires the elimination of oxygen atoms to get linear hydrocarbons. Hydrogenation is the main catalytic process to produce linear hydrocarbon by reacting the vegetable oils with hydrogen in the presence of a heterogeneous catalyst [2]. Using noble metals makes this process expensive and non-sustainable with a negative impact to the environment [3–5]. For this reason, the use of non-noble metals as catalytic active species is a very promising step in the right direction.

Using copper as active species in supported catalysts for biomass transformation is attractive for several reasons. These metal species reduce the formation of coke on the catalytic materials avoiding its deactivation [6, 7]. Cu catalytic sites are active and highly selective to desired products in hydrogenation processes [8]. It was also used in combination with noble metals such as Re or Au to increase the catalytic performance [9, 10]. It is a more environmental-friendly and inexpensive active phase compared to others. On the other hand, mesoporous ordered materials have been developed and used for several applications, including heterogeneous catalysis [11, 12]. Cu supported catalysts on mesoporous silica have been employed with superior catalytic behavior in several processes such as oxidation [13] hydrogenolysis of dimethyl maleate [14] and removing effectively several dyes [15]. To the best of our knowledge, mesoporous silica KIT-5 has not been used as a support for Cu heterogeneous catalysts in the hydrogenation of fatty acids. The cubic well-defined

✉ Diego Valencia, dvalencia@imp.mx | ¹Dirección de Investigación en Transformación de Hidrocarburos, Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas Norte 152, Col. San Bartolo Atepehuacan, C.P. 07730 Mexico City, Mexico.

pore arrange of this support might be useful for biomass transformation processes. Here, we prepared a new Cu-based catalytic materials supported on KIT-5 mesoporous silica by changing the precursor of Cu^{2+} in the impregnation aqueous solution.

2 Experimental

2.1 Synthesis

KIT-5 was synthesized according to the procedure reported elsewhere [16]. We used the copolymer Pluronic® F127 (Sigma-Aldrich) as a template. The hydrothermal synthesis was carried out at 100 °C for 48 h. The template was removed by calcination under air atmosphere at static conditions at 550 °C for 4 h. The catalysts were prepared by wet impregnation of a Cu-containing water solution. We used three distinct salt with Cu^{2+} for the impregnation into the support. Those were CuCl_2 (Sigma-Aldrich, 97%), $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich) or $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Sigma-Aldrich, > 99%). The nominal composition was 7 wt. % of CuO in the KIT-5 for all the salt precursor. The catalytic materials were dried overnight at room temperature, and then they were calcined at 500 °C for 4 h under air atmosphere. These materials were reduced under a continuous flux of 15 mL min^{-1} of H_2 at 400 °C for 3 h and then the temperature decreased to room temperature. This reduction step is necessary to produce metallic Cu supported particles. Those final materials were tested as Cu/KIT-5 catalysts.

2.2 Characterization of materials

The catalysts were characterized by nitrogen physisorption, powder X-ray diffraction (XRD), UV-Vis Diffuse reflectance spectroscopy (DRS), temperature-programmed reduction (H_2 -TPR) and Fourier Transform Infrared (FT-IR) spectroscopy with pyridine. Nitrogen adsorption-desorption isotherms were measured with a Micromeritics ASAP 2405 automatic analyzer at liquid N_2 temperature. Prior to the experiments, the samples were degassed ($p < 10^{-1}$ Pa) at 473 K for 1 h. XRD patterns were recorded in the 4°–80° range on a Siemens D500 diffractometer, using Cu K α radiation ($\lambda = 1.5405$ Å) and a goniometer speed of 0.02° (2 θ) min^{-1} . The crystallite size (D) was estimated from the full width at half the maximum intensity (FWHM), using the Scherrer equation and the Jade 2010 software. The UV-Vis DRS studies were carried out in a Thermo-Scientific Evolution model 600 spectrometer. H_2 -TPR experiments were performed using a ZETON Altamira model AMI-200 with a reduction mixture of hydrogen/argon (10 vol. % of H_2) with a standard thermal conductivity detector (TCD). Surface

acidity was studied by FT-IR using pyridine as a probe molecule. The spectra were recorded on a THERMO-NICOLET model 8700 instrument. Prior to the experiments the samples were degassed under vacuum at 600 °C to evacuate all the molecules adsorbed on the materials.

2.3 Catalytic test

The catalysts were tested in the hydrogenation of palmitic acid (PA), Sigma Aldrich > 99%. 0.1 g of reduced catalyst was used for each test with 40 mL of a solution containing PA (39 mM) in *n*-dodecane (Sigma Aldrich, anhydrous > 99%), and *n*-eicosane (Sigma Aldrich, 99%) was used as an internal standard. The catalysts were tested in a Parr reactor at 280 °C and 5.2 MPa of H_2 pressure during 6 h. The course of the reaction was followed by withdrawing aliquots each hour and analyzing them on a gas chromatograph equipped with a FID. Product identification was analyzed on a Hewlett Packard GC-MS instrument.

3 Results and discussion

3.1 Characterization of materials

Figure 1 shows the adsorption-desorption isotherms of KIT-5 and its supported Cu-based catalysts. The shape of the isotherms corresponds to the type IV, with a H1 hysteresis loop. These isotherms are characteristic for the ordered mesoporous materials such as KIT-5. This indicates that the parent cubic mesoporous structure is maintained after the preparation of the CuO supported materials. The

Fig. 1 N_2 adsorption-desorption isotherms of (black filled square) KIT-5, (empty square) CuCL, (empty circle) CuNT and (empty triangle) CuSU

adsorbed volume of N_2 showed a decrement for the catalysts respect to pure KIT-5. This is in agreement due to the surface coverage of the metal particles at the surface of KIT-5. It seems that the use of different Cu^{2+} precursors do not change the structure of the support. The textural characteristics of the support and catalysts are shown in Table 1. The support exhibited the largest BET surface (S_{BET}) and micropore (S_{μ}) areas $793 \text{ m}^2/\text{g}$ and $170 \text{ m}^2/\text{g}$, respectively. These two values decreased for the Cu supported catalysts. The values for S_{BET} and S_{μ} are the largest for the precursor $CuCl_2$ impregnated into KIT-5 (484 and $68 \text{ m}^2/\text{g}$, respectively). The values of the S_{BET} for the catalysts impregnated with nitrate or sulfate are very similar. The total pore and micropore volume (V_{μ}) also decreased after the preparation of the catalysts compared to pure KIT-5.

Powder X-ray diffraction (XRD) patterns of KIT-5 and its CuO or Cu supported materials are shown in Fig. 2. KIT-5 exhibited a broad band between 15° and 35° , which is attributed to amorphous silica. After the impregnation and calcination of the Cu^{2+} salts, we detected the presence of crystalline phases due to the agglomeration of particles at the surface of KIT-5. We detected the presence of the same crystalline structure for chloride and nitrate precursors,

while sulfate showed a different diffraction peak. These crystalline structures were identified as CuO, with a monoclinic crystal system (JCPDS 1-080-1916), for the materials impregnated using Cl^- and NO_3^- as counterions. On the other hand, we identified as $CuSO_4$ with orthorhombic crystal system (JCPDS 12-0779) for the case of SO_4^{2-} salt. The nitrate or chloride precursors are similar due to the formation of similar crystalline structures at the surface, which might be related to the metal-support interactions established during the incorporation of the Cu species into the support KIT-5. On the other hand, the chemical environment when copper sulfate was used changed due to the stabilization of $CuSO_4$ at the surface of KIT-5. The formation of such crystalline phases means that the aqueous precursor change the chemical structure of the Cu species on the KIT-5, more specifically when using sulfate. We characterized the samples after the reduction of CuO to Cu supported materials, where all the species were transformed into metallic Cu at the surface of KIT-5. Calculation of the crystalline size showed quantitative differences due to the Cu^{2+} precursor used for impregnation (Table 2). The crystalline size is the biggest for the catalysts impregnated with chloride, while the smallest was found when using

Table 1 Textural characteristics of KIT-5 and its Cu supported catalysts

Sample	Precursor ^a	S_{BET} ^b (m^2/g)	S_{μ} ^c (m^2/g)	V_p ^d (cm^3/g)	V_{μ} ^e (cm^3/g)	D_p ^f ($\text{\AA}$)
KIT-5	–	793	170	0.568	0.072	29
CuCL	$CuCl_2$	484	68	0.396	0.027	33
CuNT	$Cu(NO_3)_2 \cdot 3H_2O$	459	58	0.394	0.023	34
CuSU	$CuSO_4 \cdot 5H_2O$	461	43	0.407	0.016	35

^a Cu^{2+} salt used in aqueous solution for the impregnation to KIT-5

^bSpecific surface area determined by the BET method

^cMicropore area estimated using the correlation of t-plot method

^dTotal pore volume determined by nitrogen adsorption at a $p/p^0 = 0.98$

^eMicropore volume determined by the t-plot method

^fPore diameter corresponding to the maximum of the pore size distribution calculated from the desorption isotherm by the BJH method

Fig. 2 Powder X-ray Diffraction (XRD) patterns for Cu supported catalysts as **A** oxide and **B** reduced forms. (a) KIT-5, (b) CuCL, (c) CuNT and (d) CuSU. Crystalline systems detected: black filled square CuO (JCPDS 1-080-1916), empty circle $CuSO_4$ (JCPDS 12-0779) and black filled circle Cu (JCPDS 4-0836)

Table 2 Crystalline size of the oxide (D_O) and reduced (D_R) catalytic materials

Catalyst	D_O (Å)	D_R^c (Å)
CuCL	817 ^a	1000
CuNT	663 ^a	738
CuSU	488 ^b	596

^aCrystalline size of CuO calculated from the XRD data from the (111) plane

^bCrystalline size of CuSO₄ calculated from the XRD data from the (121) plane

^cCrystalline size of Cu calculated from the XRD data from the (111) plane

sulfate. The effect of the reduction step on the crystalline size formed larger crystals at the surface of KIT-5. This was found for all the materials, this might be correlated with sinterization processes of the particles due to the thermal treatment under H₂ atmosphere.

UV-vis Diffuse reflectance spectroscopy (DRS) was used for characterizing the CuO catalysts supported on KIT-5 (Fig. 3). All the samples showed a band at 250 nm, which is associated to ligand to metal charge transfer (LMCT) of the O²⁻ to mononuclear metal center Cu²⁺ [17]. We found some shoulders for the catalyst prepared with chloride and nitrate at about 300–350 nm, also associated with LMCT of binuclear complexes Cu–O–Cu [18]. This small shoulder is not present in the catalyst prepared with sulfate, which is in good agreement with the distinct chemical species due to the counter ion. The catalysts showed more differences in the bands for the d-d

transition located at 600–800 nm. The increase of the band at 750 nm pointed out that the catalysts prepared with CuSO₄ exhibited more species in pseudo-octahedral coordination [19]. It seems that nitrate and chloride counter ions formed more than only one species than sulfate due to the band at about 300–350 nm. The nature of the counter ion used for the impregnation of Cu²⁺ species into the support KIT-5 provides differences in the species formed within the supported particles. We found differences in the Cu species supported on KIT-5 due to the change in the salt precursor used in the impregnation solution. This is remarkable since a simple change in the salt used has consequences in the supported particles, which can be tuned properly to achieve desired properties for preparing novel catalytic materials for biomass conversion.

Temperature-programmed reduction (H₂-TPR) experiments were conducted to investigate the dispersion of CuO on KIT-5 (Fig. 4). These experiments are related to the reduction in the supported catalytic materials as follows: CuO + H₂ → Cu + H₂O. Therefore, this technique also allowed us to compare the capability of the Cu species to form the reduced species due to the counter ion used for impregnation. We found that CuCL catalyst showed two main peaks located at 260 and 504 °C. These peaks mean that the two types of particles are present in the catalyst, one with strong interaction (high temperature peak) and other in weak interaction or well dispersed on the support (low temperature peak) [20, 21]. We found the presence of two peaks for the CuNT catalyst, but a shift in temperature is remarkable. The low temperature peak appears at 250 °C and the high temperature one at 391 °C. The catalysts prepared with CuSO₄ exhibited also the same behavior under

Fig. 3 UV-vis DRS for (a) CuCL, (b) CuNT and (c) CuSU **Fig. 4** H₂-TPR profiles for (a) CuCL, (b) CuNT and (c) CuSU

H₂-TPR experiments, but with a predominant main reduction temperature. The low temperature peak is located at 300 °C and a small shoulder very close at 377 °C. This is in good agreement with UV–Vis DRS results where one predominant Cu species was found when using sulfate as counter ion. The reduction profiles of the CuO species supported on KIT-5 pointed our differences in the dispersion depending on the aqueous precursor. The impregnation of the Cu species with nitrate seems to produce well dispersed particles due to the low temperature peak. Chloride precursor produces poorer dispersion of the particles because of the high intensity peak at high temperature (504 °C). On the other hand the impregnation with CuSO₄ favors the formation of one species predominantly and this is in good agreement with the UV–vis DRS results. In this line, the low reduction peak for the catalyst CuNT might increase the formation of metallic Cu, necessary as the active species in the hydrogenation catalytic reaction of biomass feedstocks.

The catalysts were further studied by Fourier Transform Infrared (FT-IR) spectroscopy using pyridine as a probe molecule. The spectra after adsorption and degasification of pyridine at 100 °C are displayed in Fig. 5. The analyzed range in the IR region (1400–1700 cm⁻¹) showed the vibration of the bonds forming the heterocyclic molecule. These bands appeared as a consequence of the adsorption of pyridine in distinct acid sites. Two absorption bands are detected at 1446 and 1450 cm⁻¹ due to the coordination of pyridine with Lewis acid sites. These sites are correlated with Cu catalytically active centers [22]. The catalysts prepared with nitrate or chloride exhibited similar Lewis acid sites (1450 cm⁻¹), while the catalyst prepared with sulfate showed a shift in the position of the IR band (1446 cm⁻¹).

Fig. 5 FT-IR after adsorption/desorption of pyridine on the reduced catalysts at 100 °C: (a) CuCL, (b) CuNT and (c) CuSU

This shift might suggest different strength in the Lewis sites, being weaker for the Cu catalysts impregnated with sulfate. On the other hand, we found another common IR band at 1606 cm⁻¹ for all the catalysts, which is ascribed to Lewis acid sites. This band is more pronounced for the catalysts impregnated with nitrate or chloride while a tiny peak is detected for the material prepared with sulfate. We found a clear band at 1595 cm⁻¹ in the catalysts prepared with sulfate, which is associated to weaker Lewis acid sites [23]. We detected small presence of Brønsted acid sites in all the materials. For instance, the bands located at 1550 and 1576 cm⁻¹ are associated with the formation of the pyridinium ion [24], those are more pronounced for the catalyst prepared with sulfate, which is in good agreement with the chemical nature of this counter ion. This Brønsted acid site is null for the catalysts prepared with nitrate or chloride. These results showed the differences in the chemical species of Cu due to the precursor used during the impregnation step.

The bands obtained from the FT-IR spectra were deconvoluted and then integrated to obtain the concentration of pyridine on each acid site. Brønsted (B) and Lewis (L) acid sites were calculated from the bands at 1550 and ~1448 cm⁻¹, respectively [25]. The concentration of pyridine adsorbed on the materials revealed that Lewis acidity is present in all the materials (Table 3). This result is consistent with the acidity provided mostly by Cu sites. We found that the CuSU catalyst has a combination of Lewis and Brønsted acid sites with larger proportion of weaker Lewis sites. It is important to note that the catalysts prepared with nitrate showed the major amount of acid sites in this catalysts series (616 μmol/g).

3.2 Catalytic test

The Cu/KIT-5 catalysts were tested in the hydrogenation of palmitic acid. This model compound represents a range of linear fatty acids, which are present in biomass feedstocks. The CuNT catalyst is the highest active in this series with an initial rate of hydrogenation reaction of $4.5 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$, while this kinetic parameter over the CuCL and CuSU catalysts is very similar between them ($0.3 \times 10^{-2} \text{ mol L}^{-1} \text{ h}^{-1} \text{ g}_{\text{cat}}^{-1}$). The conversion of palmitic

Table 3 Concentration of pyridine (μmol/g) adsorbed on the Cu/KIT-5 catalysts. Distinction between Brønsted (B) or Lewis (L), total acid sites and mole fraction (X)

Catalyst	B (μmol/g)	L (μmol/g)	Total (μmol/g)	X _B	X _L
CuCL	0	333	333	0.00	1.00
CuNT	0	616	616	0.00	1.00
CuSU	11	510	521	0.02	0.98

acid at 6 h is also enlisted in Table 4. We can expect very little kinetic values due to the poor dispersion of the Cu in the KIT-5 in the case of chloride detected by UV-vis DRS and H₂-TPR. However, the CuSU catalyst showed dispersed species on the KIT-5 support, but this material formed CuSO₄ on the support's surface. Additionally, we found the formation of mostly one Cu species in pseudo-octahedral symmetry by UV-vis DRS and H₂-TPR in this catalyst and a combination of Brønsted and weaker Lewis acid sites. This very selective formation of one predominant species of Cu in KIT-5 is not a positive effect on its catalytic performance. We also found that the reduction temperature of CuO species in the CuNO catalyst is the lowest, then the formation of metallic Cu species is the highest, producing the highest active metallic catalyst in this series. This catalysts exhibits the highest amount of Lewis acid sites in this series, this type of active sites are also a positive effect in its performance. The high dispersion of Cu particles, the formation of two species and the largest acid strength in the CuNT catalyst might be responsible for the high catalytic activity.

We also analyzed the products formed in the hydrogenation of palmitic acid over these Cu-based catalysts (Scheme 1). The composition of products are displayed in Table 4. The products formed using CuCL or CuNT catalysts are very similar, mostly 1-hexadecanol and *n*-hexadecane, the products from the hydrogenation processes. The CuCL catalyst is extremely selective to produce 1-hexadecanol without any other byproduct. This is an interesting

catalyst to achieve higher yields of fatty alcohols in the partial reduction reaction. We detected also higher formation of 1-hexadecanol (96%) and also the product of the hydrodeoxygenation (HDO), *n*-hexadecane (4%), by using CuNT catalyst. Interestingly, we found a different distribution when the CuSU catalyst was employed. We detected the presence of hexadecanal, *n*-pentadecane and 1-pentadecene. These products are formed by different reaction mechanisms, where dehydrogenation reactions take place over this material. Although the conversion of palmitic acid over CuCL or CuSU catalysts is very similar, the selectivity is very different. The catalyst CuSU produces more O-free compounds and it reacts towards dehydrogenation reactions. We found the presence of CuSO₄ compound at the surface of the support by XRD. We also found the formation of both Lewis and Brønsted acid sites due to Cu and sulfate species, respectively. Then, the distribution of products of palmitic acid over this catalyst is a consequence of the combination of these distinct active sites. The sulfate species might be responsible for acidic surface properties that can promote dehydrogenation reactions of the biomass derived compounds. Therefore, the nature of the precursor used in the impregnation solution has consequences in the chemical characteristics and catalytic performance of the Cu/KIT-5 catalysts. This feature can be exploited by tuning properly the precursor used in the impregnation solution to synthesize active and selective heterogeneous catalysts in biomass conversion.

Table 4 Kinetic parameters and relative composition of products over the Cu/KIT-5 catalysts

Catalyst	Conversion at 6 h (%)	$r_0 \times 10^{-2}$ (mol L ⁻¹ h ⁻¹ g _{cat} ⁻¹) ^a	Products (%)				
			hexadecanal	1-hexadecanol	<i>n</i> -hexadecane	<i>n</i> -pentadecane	1-pentadecene
CuCL	21	0.3	–	100	–	–	–
CuNT	82	4.5	–	96	4	–	–
CuSU	22	0.3	21	–	–	45	34

^aInitial rate of reaction

Scheme 1 Reaction network in the hydrogenation of palmitic acid (R=C₁₄H₂₉; R₂=C₁₃H₂₇). R-CH₂-COOH=Palmitic acid, R-CH₂-COH=hexadecanal, R-CH₂-CH₂OH=1-hexadecanol, R-CH₂-CH₃=*n*-hexadecane, R-CH₃=*n*-pentadecane and R₂-CH=CH₂=1-pentadecene

4 Conclusions

New Cu-based catalysts supported on KIT-5 were successfully synthesized by varying the metal precursor used in the impregnation solution. These Cu/KIT-5 catalysts can be an attractive alternative for the production of sustainable fuels over sustainable materials. Changing the metal precursor in aqueous solutions modified the metal species impregnated to the support. We found the formation of CuO or CuSO₄ on the support's surface depending on the salt employed. Different Cu²⁺ species are formed on the support due to the metal-support interaction established by changing the aqueous precursor. The biggest particles were found when using copper chloride for the impregnation into KIT-5. The catalytic materials exhibited Lewis acid sites with larger amount for the catalyst prepared with nitrate, while tiny amount of Brønsted acid sites were detected when using sulfate. The highest catalytic activity was achieved with copper nitrate salt for impregnation, where Cu binuclear and pseudo-octahedral symmetries with higher reactive Lewis acid sites were found. The catalytic activity when using chloride or sulfate decreased significantly. However, both catalysts provide different reaction networks. Therefore, the use of Cu as an active phase with KIT-5 is promising in biomass transformation by varying the molecular species for the synthesis of the materials.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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