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# Syngas conversion to ethanol over a mesoporous Cu/MCM-41 catalyst: effect of K and Fe promoters

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#### **Graphical abstract**



#### **Highlights:**

- The effect K and Fe as metal promoters on mesoporous Cu/MCM-41 catalyst is studied.
- K favors the formation of oxygenates and Fe favors the formation of hydrocarbons.
- The combination of K and Fe on the Cu/MCM-41 catalyst notably increases the ethanol yield.

#### Abstract

Transportation fuels such as ethanol can be obtained through thermochemical processing of biomass. Interest in the development of more selective catalysts for the conversion of biomass-derived syngas (H<sub>2</sub>+CO) to ethanol is increasing in both academia and industry. In this work, we have evaluated the performances of K and Fe as metal promoters of a mesoporous Cu/MCM-41 catalyst and their effects on the product selectivity and especially on ethanol formation. The metal loading was 29 wt.% Cu, 2 wt.% Fe and 1.6 wt.% K. The catalysts were tested at 300 °C, 20 bar and gas-hourly-space-velocities in the range of 1500-30000 ml<sub>syngas</sub>/g<sub>cat</sub> h; under these conditions the syngas conversion level was between 2 and 11%. The nonpromoted Cu/MCM-41 catalyst showed interesting selectivity toward oxygenated compounds, mostly methanol. The addition of K as promoter increases the selectivity toward methanol even more, while the addition of Fe as promoter favors the formation of hydrocarbon compounds. When both K and Fe as promoters are incorporated into the Cu/MCM-41 catalyst, the reaction rate to oxygenated compounds is notably increased, especially for ethanol. The space time yield for ethanol for the Cu/MCM-41 catalyst is 0.3x10<sup>-5</sup> carbon-mol/g<sub>cat</sub>h which increases to 165.5x10<sup>-5</sup> carbon-mol/g<sub>cat</sub>h for the Cu-Fe-K/MCM-41 catalyst. From XPS analysis, the Cu-Fe-K/MCM-41 catalyst was found to have the following atomic composition: Cu<sub>0.34</sub>Fe<sub>0.08</sub>K<sub>0.08</sub>Si<sub>1.00</sub>. The promoting effect of both K and Fe, may be related to an increased reaction rate toward CO non-dissociation and CO-dissociation paths, respectively, which is beneficial for the ethanol formation. Further catalytic results, catalyst characterization and discussion of results are presented in this work.

Keywords: copper, ethanol, mesoporous MCM-41, promoters, syngas.

#### 1. Introduction

During the last few years, biofuels have become an important renewable fuel for the transportation sector. Biofuels are gaseous or liquid fuels obtained from the processing of renewable resources such as biomass. Biomass includes forest and agricultural biomass, industrial waste streams and municipal solid waste. Almost all kinds of biomass can be converted to useful fuels via the thermochemical route [1], in which the primary biomass is gasified to produce a mixture of gases know as synthesis gas (syngas) formed by hydrogen, carbon monoxide and a minor amount of carbon dioxide. The syngas is thereafter catalytically converted to the desired fuel, such as FT diesel, SNG (synthetic natural gas), ethanol and others using a heterogeneous catalyst.

Ethanol grade fuel constitutes most of the biofuels consumed today. World ethanol production is forecast to increase from about 100 billion liters in 2013 to 158 billion liters in 2023 [2]. The thermochemical approach may become an important route for producing ethanol from biomass for large-scale production. The gasification of biomass is the most studied technology for producing syngas, where some aspects inherent to biomass are being evaluated, such as contaminants like chlorine, sulfur and alkali metals [1]. Several kinds of catalysts have been tested for the conversion of syngas to ethanol and higher alcohols (C<sub>2+</sub>-OH) [3-5], among

which the Rh, Mo and Cu-based catalysts are the most promising up to date. Nevertheless, further research is needed to gain insights into the conversion of syngas to ethanol, which will allow designing a more selective and active catalyst.

It has been found that the catalyst support has an important role in the synthesis of ethanol and higher alcohols. For example, silica support is beneficial for alcohol formation, which seems to be due to a different surface composition of the adsorbed CO as compared to on other catalyst supports [3]. Silica meso-structured support, such as MCM-41, is a novel material with high surface area (around 1000 m<sup>2</sup>/g), which can be used to improve the dispersion of the active sites. In previous works, we have used MCM-41 as support for a Rh-based catalyst with interesting results [6, 7]. To the best of our knowledge, there are no other studies using MCM-41 as support for Cu-based catalysts. In order to increase the selectivity to ethanol and higher alcohols the Cu-based catalysts are promoted by, for example, alkali and transition metals [3-5]. Potassium, K, as a promoter has been successfully used to improve the selectivity to higher alcohols over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts [8, 9]. Another metal promoter with good results for alcohols formation is Fe, which facilitates the carbon chain growth similarly as occurs in the Fischer-Tropsch synthesis [1]. Thus, a combination of K and Fe promoters would be beneficial for both ethanol and higher alcohols formation.

The synthesis of higher alcohols is, to some extent, similar to the Fischer-Tropsch Synthesis (FTS) where chain polymerization occurs to form mostly hydrocarbon compounds [10]. The FTS is in part described by the model of Anderson-Shultz-Flory (ASF), defined by equation (1) [10, 11]:

$$\frac{S_n}{n} = \alpha^{n-1} (1-\alpha)^2 \tag{1}$$

$$ln\left(\frac{s_n}{n}\right) = ln\frac{(1-\alpha)^2}{\alpha} + ln(\alpha)n \tag{2}$$

where  $S_n$  is the selectivity to molecules with n carbon atoms and  $\alpha$  is the chain growth propagation probability (independent of n). The value of  $\alpha$  is obtained by least-square linear regression of the logarithmic form of the ASF equation (2). The chain growth propagation probability  $\alpha$  is directly related to the rate of chain propagation and inversely to the rate of chain termination.

In this work, we have evaluated the catalytic performance of the following catalysts: Cu/MCM-41, Cu-Fe/MCM-41, Cu-K/MCM-41 and Cu-Fe-K/MCM-41. Various characterization techniques (XRD, N<sub>2</sub> physisorption, TEM, TPR, ATG and XPS) were employed to examine the physico-chemical properties of the prepared catalysts. The catalytic experiments indicate that the incorporation of Fe-K into the Cu/MCM-41 catalyst favors the selectivity to oxygenated compounds and, more interestingly, the space time yield for ethanol increases notably.

#### 2. EXPERIMENTAL

#### 2.1. Catalyst Preparation and Characterization Techniques

For the preparation of the catalyst support, the "atrane route" [34] was used to obtain a hexagonal mesoporous silica, type MCM-41, where cetyltrimethylammonium bromide was used as the structural directing agent. A characteristic of this method is the use of a hydrolysis-retarding agent such as triethanolamine (TEA). TEA and tetraethyl orthosilicate were mixed to obtain silatrane complexes, which are the precursors of Si. Further preparation procedures are described elsewhere [34,35]. The addition of Cu onto MCM-41 was done by aqueous wetness impregnation using an excess of water under constant stirring for 3 h. After impregnation, the sample was dried at 120 °C for 3 h and then calcined at 500 °C for 5 h to obtain the Cu/MCM-41 catalyst. Subsequently, K was added to the Cu/MCM-41 catalyst following the same procedure as for Cu addition and using the same thermal treatment (described above). Then, Fe was added to the Cu-K/MCM-41 catalyst also following the same procedure as for the Cu addition and the same thermal treatment. The metal precursors used were Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and K<sub>2</sub>CO<sub>3</sub> purchased from Sigma-Aldrich.

Powder X-ray diffraction (XRD) was performed in a Siemens D5000 instrument using Cu K- $\alpha$  radiation (20=10-90°, step size=0.04°) equipped with a Ni filter and operated at 40 kV and 30 mA. The metal loading was estimated by atomic absorption spectroscopy in a Perkin Elmer AAnalyst 200, for which the samples were dissolved in HF (40%) for 48h at ambient temperature. N<sub>2</sub> physisorption was carried out in a Micromeritics ASAP 2000 instrument. The Brunauer-Emmett-Teller (BET) method was used to estimate the specific surface area and the Barrett-Joyner-Halenda (BJH) method was used to estimate the pore size and pore volume from the desorption isotherm. Temperature programmed reduction (TPR) was performed in a Micromeritics Autochem 2910 instrument; a reducing gas mixture formed by 5% H<sub>2</sub>/Ar was passed through the catalyst sample at a flow of 50 ml/min while the sample temperature was increased by 5 °C/min up to 900 °C. Thermogravimetric analysis (TGA) was carried out using a SETARAM STA (TG-DTA-DSC 1600 °C); a continuous flow of He was passed through the sample during the analysis. The sample was heated up to 400 °C at a rate of 5 °C/min. The differential thermogravimetric (DTG) curves were estimates from the TGA data.

Transmission electron microscopy (TEM) images were collected using a JEOL JEM 1400 microscope. All samples were mounted on 3 mm holey carbon copper grids. The particle size and distribution were estimated by examination of more than 100 metal particles. X-ray photoelectron spectroscopy (XPS) data were recorded using a Leybold-Heraeus LHS10 spectrometer as the main chamber, capable of operating down to  $2 \cdot 10^{-9}$  Torr, which was equipped with an EA-200MCD hemispherical electron analyzer with a dual X-ray source using AlK $\alpha$  (hv=1486.6 eV) at 120 W, 30 mA, with C(1s) as energy reference (284.6 eV). The powder samples were gently pressed to form pellets of 4 mm × 4 mm and 0.5 mm thickness, followed by outgassing to a pressure below  $2 \cdot 10^{-8}$  Torr at 150 °C to remove chemisorbed volatile species. For TEM and XPS analyses the catalyst samples were previously reduced in a flow of 50 ml/min H<sub>2</sub> and heated at 5 °C/min up to 370 °C and kept at this temperature for 60 min.

#### 2.2. Catalytic Testing

The catalytic testing was carried out in a stainless-steel, down-flow fixed bed reactor. The internal diameter of the reactor was 8.3 mm and the system components have been described by Andersson et al. [12]. About 200 mg of the catalyst sample with a particle size of 160-250 µm was charged into the reactor. Before the reaction,

the catalysts were reduced under pure hydrogen flowing at 50 ml/min and heated at a rate of 5 °C/min up to 370 °C and kept at this temperature for 60 min. Then, the reaction conditions were fixed to 300 °C and 20 bar. The gas hourly space velocity (GHSV) was varied between 1500 and 30000 ml<sub>syngas</sub>/g<sub>cat</sub> in order to maintain the reaction conversion at less than 11% and thus avoid mass-transfer limitations. All the experiments were made with a syngas ratio of H<sub>2</sub>/CO = 2/1.

The reaction products were analyzed using a gas chromatograph (Agilent GC-7890A) connected on-line to the catalytic reactor. A detailed description of the GC configuration and the analytical procedure can be found elsewhere [12]. N<sub>2</sub> was mixed with syngas which acted as internal standard to quantify the smaller gases (CH<sub>4</sub>, CO and CO<sub>2</sub>) using a thermal conductivity detector. For the larger gaseous compounds, two flame ionization detectors (FIDs) were used, one for non-polar gases (hydrocarbon compounds) and the other for the polar gases (oxygenated compounds). The internal normalization of corrected peak areas method was used to quantify the hydrocarbon and oxygenated compounds in both FIDs [13]. From these results; the syngas conversion, carbon-mole selectivity and carbon balance were calculated using the equations shown in reference [12]. In all the experiments the carbon balance was in the range of 99.4-100%.

#### 3. RESULTS AND DISCUSSION

#### 3.1. Catalyst Characterization

#### 3.1.1. Powder X-ray diffraction (XRD)

The X-ray diffraction patterns of the prepared catalysts are shown in Figure 1. After Cu impregnation, the signals observed at 35.6\*20 and at 38.8\*20 correspond to CuO when compared to the powder diffraction of standard compounds reported in JCPDS (No. 05-661). The addition of K and Fe does not generate new signals, this could probably be due, in part, to the small amounts used in the impregnation (3%wt. K and 1.6%wt. Fe) and, in part, be due to highly dispersed aggregates of K and Fe, resulting in no appreciable signals using the XRD technique.

#### 3.1.2. N<sub>2</sub> physisorption

Table 1 summarizes the results from N<sub>2</sub> physisorption for the prepared catalysts. It can be noted that the mesoporous MCM-41 support has a large surface area. The high surface area of the MCM-41 support is due to the small 1D channel porous structure which is interconnected by a thin wall thickness of around 0.8 nm [14]. The pore size of the prepared MCM-41 corresponds to the mesoporous range, i.e. 2.9 nm (Table 1). Moreover, when the metals (Cu, K and Fe) are impregnated onto MCM-41 the surface area decreases. This suggests a structure degradation possibly due to 1D pores collapsing during the catalyst preparation. The structure degradation of MCM-41 during catalyst preparation has been also observed by Landau et al. [15]. In our catalysts, the structure degradation is less noticeable in the Cu/MCM-41, Cu-K/MCM-41 and Cu-Fe/MCM-41 catalysts and more notable in the Cu-Fe-K/MCM-41 catalysts.

#### 3.1.3. X-ray photoelectron spectroscopy (XPS)

Atomic ratios obtained from the XPS technique are included in Table 1. The Cu/MCM-41 catalyst has a Si/Cu ratio of 2.8, which is slightly increased to 2.9 when K is incorporated into the catalyst (Cu-K/MCM-41). When Fe is incorporated (Cu-Fe/MCM-41) the Si/Cu is increased to 7.0, which may suggest that Fe atoms cover some Cu particles or that some Cu atoms migrate from the outside to the core of the catalyst particle. Finally, when both K and Fe are incorporated (Cu-Fe-K/MCM-41) the Si/Cu ratio is remains at 2.9, suggesting that K favors the dispersion of Cu on the catalyst's surface. This can be related to some reports suggesting that K stabilizes some Cu sites, presumably Cu<sup>+</sup> species [16, 17].

Figure 3 shows the Cu2p-spectra of the prepared catalysts. The presence of the metal promoters do not modify the oxidation state of copper since the characteristics peaks,  $Cu2p_{3/2}$  (932.5 eV) and  $Cu2p_{1/2}$  (952.2 eV), remain in the same position in all the catalysts. These signals can be attributed to either Cu<sup>0</sup> or Cu<sup>+1</sup> [18], which can be related to the active sites for the catalytic conversion of syngas, and in particular for the methanol synthesis [19]. There are not signals of any satellite in the range 940-945 eV, indicating that CuO is not present in the prepared catalysts [18]. The binding energy for each element in the catalysts is: Si=103.2 eV, O= 532.5-532.7 eV, Cu=932.4-932.6 eV, K=293.0-293.2 eV and Fe=711.3 eV.

#### 3.1.4. Transmission electron microscopy (TEM)

Figure 4 shows the TEM images of the prepared catalysts. From these images it can be noted that the incorporation of Fe and K onto the Cu/MCM-41 catalyst does not drastically change the morphology of the catalyst. This can be related to the low amount of Fe and K used in the catalyst preparation. Moreover, the average of the metal particle size is about 5 nm for the Cu/MCM-41, Cu-K/MCM-41 and Cu-Fe/MCM-41catalysts and it is slightly increased to 6 nm for the Cu-Fe-K/MCM-41 catalyst (see Table 1). The average of the particle size takes in account the contribution of all the metals present in the catalysts.

#### 3.1.5. Temperature-programmed reduction (TPR)

Figure 5 shows the TPR profiles of the prepared catalysts. The reduction temperature is centered at around 245 °C with a shoulder at 220 °C for the Cu/MCM-41 catalyst. The shoulder in TPR may indicate the formation of strong metal-support interactions, which affect the reduction of the metal oxide [20], also reported for mesoporous catalysts [21]. When K is added, a single reduction peak is observed which is decreased to around 210 °C (Cu-K/MCM-41). It seems that the presence of K partially eliminates or weakens some metal-support interactions between Cu and the MCM-41 support. In the Cu-Fe/MCM-41 and Cu-Fe-K/MCM-41 catalysts a reduction peak centered at 335 °C and 350 °C, respectively, is observed. This reduction peak can be attributable to the reduction of oxidized species of Fe, possibly Fe<sub>2</sub>O<sub>3</sub>  $\rightarrow$  Fe<sub>3</sub>O<sub>4</sub> [22]. In both catalysts a shoulder at 295 °C is observed which can be attributed to the reduction of CuO, thus CuO in Fe-containing catalysts is reduced at higher temperature than for the Cu/MCM-41 catalyst. The latter may be due to some electronic effects induced by the presence of Fe.

#### 3.1.6. Thermogravimetric analysis (TGA)

The thermograms of the prepared catalysts are shown in Figure 6. The mass loss in the range of 20-152 °C can be attributed to the process of elimination of physisorbed water (dehydration) from the surface of the

catalysts. This mass loss represents about 3.0-5.9 wt.%. A large tail of this process is observed in all the catalysts; it can be ascribed to the elimination of surface hydroxyl groups (dehydroxylation) heterogeneously distributed on the catalyst surface [23]. The mass loss of the dehydroxylation is about 1.5-2.5 wt.%. Besides the dehydration/ dehydroxylation processes no further changes are observed in the catalysts.

#### 3.2. Catalytic activity

#### 3.2.1. Effect of the metal promoters on the product selectivity trends

In the catalytic activity experiments, all catalysts were tested using the same syngas ratio, H<sub>2</sub>/CO=2. In Figure 7, the product selectivity trends obtained from the mesoporous catalysts are shown. The products are divided into oxygenated compounds (alcohols, aldehydes, carbon dioxide and acetates) and hydrocarbon compounds (alkanes and alkenes). If we first analyze the Cu/MCM-41 catalyst, it can be observed that the selectivity to oxygenated compounds is higher than the selectivity to hydrocarbon compounds. Reports, however, using Cu-based catalysts supported on non-porous silica show the opposite selectivity trends [24, 25] as compared to our results. Some characteristics of the prepared Cu/MCM-41 catalyst could affect to the product selectivity, such as: i) structured catalyst with an average pore size of 3.2 nm (Table 1) and ii) some metal-support interactions as suggested by the TPR analysis (Figure 5). In a previous work it was found that a mesoporous catalyst (Rh/MCM-41) catalyst. Thus, the particular product selectivity obtained for the Cu/MCM-41 catalyst could also be the case for the Cu/MCM-41 catalyst. Thus, the particular product selectivity obtained for the Cu/MCM-41 catalyst could be related to both water vapor concentration and some metal-support interactions. The concentration of water vapor occurs due to the small pore size in the mesoporous catalysts [6, 7]. Accordingly, we believe that the product distribution is less affected by the water vapor concentration in the promoted catalysts since they present collapsed pores (Figure 2) and thus minor or negligible water vapor concentration could be expected.

On the other hand, since the experiments were carried out at low syngas conversion we expect minor or negligible catalyst deactivation effects on the catalytic results. Also, a minor effect on the product distribution due to the degree of syngas conversion could be expected since the experiments were done at similar syngas conversion (2-11%).

#### a) Effect of K as promoter

Incorporation of K into the Cu/MCM-41 catalyst changes the product selectivity as can be seen in Figure 7 (Cu-K/MCM-41), where the oxygenated compounds are an even higher fraction and represent 92% of all the products. It is known that K is a good promoter for the formation of oxygenated compounds and this is related to two main functions: i) stabilizing the active sites, presumably Cu<sup>+</sup> species [16, 17]), which can be related to the lower reduction temperature of the Cu-K/MCM-41 catalyst compared to the Cu/MCM-41 catalyst as can be seen in Figure 5 and ii) blocking acid sites thus decreasing the hydrocarbons formation [26]. In addition, it was observed by TPR analysis (see section 3.1.5.) that the metal-support interactions in the Cu/MCM-41 catalyst are weakened or eliminated by the presence of K, which suggests the metal-support interactions have a minor effect on the formation of oxygenated compounds. Thus, the higher selectivity to oxygenated compounds

found over the Cu-K/MCM-41 catalyst may be mostly due to the promoting effect of K and less caused by metal-support interactions.

#### b) Effect of Fe as promoter

The incorporation of Fe into the Cu/MCM-41 catalyst changes the product selectivity as can be seen in Figure 7 (Cu-Fe/MCM-41), where the selectivity to hydrocarbon compounds increases from 16% to 54%. While the K promoter favors formation of oxygenated compounds, Fe promoter favors hydrocarbon formation. It is known that Fe is a good catalyst for the Fischer-Tropsch synthesis, where the formation of hydrocarbons is preferred. It is believed that the hydrocarbon formation occurs via CO dissociation, which can be either unassisted or H-assisted, where radicals C\* (or \*CH) are formed on the catalyst's surface [1]. The radicals then react to form C-C bonds, which after hydrogenation steps produce hydrocarbon compounds. From the XPS analysis (see Table 1) a smaller proportion of Cu was observed on the surface of the Cu-Fe/MCM-41 catalyst than on the Cu/MCM-41 catalyst, which might reduce the formation of oxygenated compounds and favor hydrocarbon formation. The presence of Fe increases the syngas conversion. In order to keep the syngas conversion to less than 11%, it was necessary to increase the gas hourly space velocity from 1500 ml<sub>syngas</sub>/g<sub>cat</sub>h for Cu/MCM-41 catalyst have higher activation energy than the Cu-K/MCM-41 catalyst (Figure 5).

#### c) Effects of Fe and K addition

The product selectivity obtained when both K and Fe promoters are incorporated into the Cu/MCM-41 catalyst is shown in Figure 7. It can be observed that the selectivity to hydrocarbon compounds (52%) is similar to the selectivity to oxygenated compounds (48%) after 20 hours on stream. It was noted previously that K as promoter favors oxygenated compounds formation, possibly via CO non-dissociation [3], while Fe as promoter favors hydrocarbon formation, possibly via CO dissociation [1]. Hence, when K and Fe promoters are present both CO dissociation and CO non-dissociation will take place. In addition, CO insertion could also take place over the Fe promoter and oxygenated compounds can be formed via the so-called enol mechanism [1]. Moreover, there is no consensus about which mechanism is the dominant [3-5], and further studies are needed to clarify the reaction mechanism for Cu-promoted catalysts. The TPR analysis of the Cu-Fe-K/MCM-41 catalysts (see Figure 5). In the next section, the product distribution between the oxygenated products will be analyzed and how the combination of both K and Fe promoters can be a good strategy for boosting the selectivity to alcohols.

#### 3.2.2. Selectivities to alcohols and other oxygenated compounds

The product distribution between the oxygenated compounds is shown in Figure 8. The oxygenated compounds are methanol, higher alcohols (C<sub>2+</sub>-Alcohols), acetates (methyl and ethyl acetate) and others (aldehydes and acetic acid). It can be noted that methanol is the dominant product (>98%) for the Cu/MCM-41 and Cu-K/MCM-41 catalysts. When Fe is incorporated into Cu/MCM-41, the methanol selectivity decreases to

45% while the selectivity to higher alcohols is increased to about 33%. Furthermore, when both K and Fe promoters are incorporated the selectivity to higher alcohols represents around 49% of all the oxygenated compounds. This indicates that the combination of these promoters with different roles, K promoting the CO non-dissociation and Fe promoting the CO dissociation, is favorable for the formation of higher alcohols.

More interesting is the increasing selectivity toward ethanol. The ethanol selectivity related to all the studied alcohols (C<sub>1-5</sub>OH) changes drastically by the action of the metal promoters. Low ethanol selectivity is found in the Cu/MCM-41 and Cu-K/MCM-41 catalysts, being 1% and 2%, respectively, while the ethanol selectivity in the Cu-Fe/MCM-41 catalyst increases to 30%. The combined Fe and K promoters in the Cu-Fe-K/MCM-41 catalyst even boost the ethanol selectivity to 41%. In addition to the ethanol selectivity being enhanced, syngas conversion is also increased, which in turn increases the ethanol yield as can be observed in Table 2. The ethanol yield for the Cu-Fe-K/MCM-41 catalyst achieves the value of 165.5x10<sup>-5</sup> C mol/ g<sub>cat</sub> h, which is notably higher than that of the non-promoted Cu/MCM-41 catalyst ( $0.3x10^{-5}$  C mol/ g<sub>cat</sub> h). Accordingly, it seems that the surface composition of the Cu-Fe-K/MCM-41 catalyst is suitable for ethanol formation, the atomic composition in this catalyst (from XPS analysis) is Cu<sub>0.34</sub>Fe<sub>0.08</sub>K<sub>0.08</sub>Si<sub>1.00</sub>. Furthermore, the ethanol formation could possibly even be increased by varying the final surface composition of Cu, Fe and K. The latter is a current subject of study in our group and future results will be published.

#### 3.2.3. Anderson–Schulz–Flory (ASF) distribution

The ASF plots for alcohols and hydrocarbon compounds are shown in Figure 9. The shapes of the curves can give qualitative information on the alcohol and hydrocarbon compounds formation; the more linear curve indicates a kind of polymerization mechanism via C<sub>1</sub> monomers with chain growth probability (*α*) independent of the carbon number (n). It can be observed that the hydrocarbon curve (HC's, dotted lines) for the Cu/MCM-41 catalyst is quite similar to the corresponding curve of the Cu-K/MCM-41 catalyst. Also, the Cu-Fe/MCM-41 catalyst shows a HC's curve similar to that of the Cu-Fe-K/MCM-41 catalyst. This suggests that two kinds of reaction mechanisms could proceed; one when Cu and K are present and another when Cu-Fe and Cu-Fe-K are present. The first mechanism favors the oxygenated compounds formation, especially methanol, as was also observed from the selectivity trends (Figures 7 and 8) which may be related to the CO non-dissociation and/or CO insertion mechanisms. The second mechanism favors the formation of hydrocarbon compounds (Figures 7 and 8) and may be related to the CO dissociation mechanism. However, further detailed studies are needed to clarify the reaction mechanism for alcohols formation over the Cu-Fe-K/MCM-41 catalyst. We believe that the various reaction mechanisms could take place in parallel resulting in a beneficial combination of CO non-dissociation, CO dissociation and CO insertion for the formation of alcohols, and particularly for ethanol formation.

#### 4. Conclusions

The catalytic performance of a mesoporous Cu/MCM-41 catalyst and the effect of K and Fe promoters were evaluated for the conversion of syngas at 300 °C, 20 bar and gas-hourly-space-velocities in the range of 1500-30000 ml<sub>syngas</sub>/g<sub>cat</sub> h, under these conditions the syngas conversion level was between 2 and 11%. The non-promoted Cu/MCM-41 catalyst produces mostly oxygenated compounds, among which methanol is the main product. When K is incorporated into the Cu/MCM-41 catalyst, the selectivity to methanol is further increased. On the other hand, when Fe is incorporated into the Cu/MCM-41 catalyst, the selectivity to hydrocarbon compounds is favored. The action of both K and Fe as promoters may be related to their effect on the reaction mechanisms. K as promoter seems to enhance the CO non-dissociation and CO insertion mechanisms to form oxygenated compounds as main products, and Fe as promoter probably enhances the CO dissociation mechanism to form hydrocarbon compounds. When both K and Fe are simultaneously present in the Cu/MCM-41 catalyst, it seems that both kinds of mechanisms (CO dissociation and non-dissociation) can take place and favor the formation of higher alcohols (C<sub>2+</sub>-OH). The reaction rate is also notably increased from 0.3x10<sup>-5</sup> carbon-mol/g<sub>cat</sub>h to 165.5x10<sup>-5</sup> carbon-mol/g<sub>cat</sub>h. From XPS, the atomic surface composition in the Cu-Fe-K/MCM-41 catalyst is Cu<sub>0.34</sub>Fe<sub>0.08</sub>K<sub>0.08</sub>Si<sub>1.00</sub>.

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Figure 1. XRD patterns of the prepared mesoporous catalysts.



Figure 2. BJH pore size distribution and (inset) N2-isotherm of the prepared catalysts.



Figure 3. Cu2p-spectra of the prepared catalysts.



Figure 4. TEM images of the prepared catalysts.





Figure 6. TGA and DTG profiles of the prepared catalysts.



**Figure 7.** Product selectivity trends obtained from the prepared catalysts. Reaction conditions: syngas H<sub>2</sub>/CO ratio: 2/1, 300 °C, 20 bar and a GHSV of 1500 ml<sub>syngas</sub>/g<sub>cat</sub> h for the Cu/MCM-41 and Cu-K/MCM-41 catalysts and 30000 ml<sub>syngas</sub>/g<sub>cat</sub> h for the Cu-Fe/MCM-41 and Cu-Fe-K/MCM-41 catalysts.



**Figure 8.** Oxygenates and alcohol selectivities obtained from the prepared catalysts. Reaction conditions as specified in Figure 7.



Figure 9. ASF plots for alcohols (OH's) and hydrocarbons (HC's) for the prepared catalysts. Reaction conditions as specified in Figure 7.

Catalyst	BET surface area (m²/g)	Pore volume (cm <sup>3</sup> /g)	Average pore size (nm)	Average metal particle size by TEM (nm)	Metal loading (%) by AAS			Atomic ratios by XPS			
					Cu	к	Fe	Si/Cu	Cu/K	Cu/Fe	Fe/K
MCM-41	710	0.49	2.9	-	-	-	-	-	-	-	-
Cu/MCM-41	375	0.24	3.2	4.8	28.89	-	-	2.8	-	-	-
Cu-K/MCM-41	208	0.26	5.1**	5.0*	29.79	1.53	-	2.9	13.0	-	-
Cu-Fe/MCM-41	200	0.32	6.6**	5.0*	26.82	-	2.28	7.0	-	4.3	-
Cu-Fe-K/MCM-41	72	0.27	14.8**	6.1*	29.30	1.65	2.07	2.9	11.7	5.3	2.2

 Table 1. Physico-chemical properties of the prepared catalysts.

\* Average of all the metals. \*\* Average of the interparticle space.

 Table 2. Space time yield (STY) of alcohols and other oxygenated compounds over the mesoporous catalysts. Reaction conditions as indicated in Figure 7.

Catalyst	Conv.	STY (10⁻⁵ C mol/ g <sub>cat</sub> h)						
Odialyst	(%)	C₁OH	C <sub>2</sub> OH	C <sub>3</sub> -C <sub>4</sub> OH	Acetates*	Others**		
Cu/MCM-41	2.2	27.3	0.3	0.0	0.0	0.2		
Cu-K/MCM-41	2.8	42.9	0.8	0.1	0.0	0.0		
Cu-Fe/MCM-41	10.0	307.2	159.2	61.4	46.4	101.8		
Cu-Fe-K/MCM-41	4.9	145.4	165.5	83.3	53.0	59.4		

\* Methyl acetate and ethyl acetate. \*\* Propanal, acetaldehyde and acetic acid.