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ZrO_2-SUPPORTED ALKALI METAL (Li, Na, K) CATALYSTS FOR BIODIESEL PRODUCTION

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ABSTRACT

We studied the effect of the alkali metal type (Li, Na, and K) and the calcination temperature (500, 600 and 700 °C) in the activity for biodiesel production of catalysts prepared by impregnation method, with constant metal content of 10%w/w using ZrO_2 as support. The results of the catalytic activity allowed to find an activity sequence regarding the alkali tested metals: Na > Li > K, with this sequence remaining constant independent of the calcination temperature. The high activity of the Na/ZrO_2 system, and slightly lower activity of Li/ZrO_2, can be explained by the fact that higher calcination temperatures promote the formation of alkali-based zirconate species, M_2ZrO_3 (M = Na or Li). The presence of these species is correlated with the higher activity of these catalysts, specifically with the Na and Li-based catalyst calcined at high temperatures (600-700 °C). These M_2ZrO_3 species show higher basicity respect to other alkali metal oxide species, as was demonstrated with CO_2-TPD results. The higher activity corresponded to 10% Na supported on ZrO_2 and calcined at 700 °C, which reached full conversion within just 30 minutes of reaction, which makes this system a promising heterogeneous replacement for the regular homogeneous systems.

Keywords: Alkali Metal, Zirconia, Heterogeneous Catalysts, Transesterification, Biodiesel

1. INTRODUCTION

The energy crisis and environmental pollution are two of the greatest problems in our current society. Consequently, biodiesel is presented as a potential substitute for fossil fuels and given its renewable nature, an alternative capable to relieve both issues.

The most common method to produce biodiesel is the transesterification reaction, where a triglyceride (compound found in vegetable oil or animal fat) reacts with a short-chain alcohol in presence of a catalyst[1]. The reaction of transesterification can be conducted using homogeneous catalysts (acid or base) and/or heterogeneous catalysts (acid or base).

Currently, the primary processes in the biodiesel industry are those using basic homogeneous catalysts (NaOH or KOH), which is due to the simplicity of the required operations and the high conversions achieved in short periods of time[2]. However, these processes present several disadvantages, such as the high amounts of waste water consumed in the removal of the corrosive catalyst and the inability of reusing the spent catalyst.

Because of the previous disadvantages, intense research is being carried out in the field of heterogeneous catalysis to find proper active replacements. The advantage of the latter is that solid catalysts are simple to prepare and it is possible to recover and reuse them multiple times. In addition, the easy recover of the catalyst greatly decrease the generation of waste cleaning water[1].

Among the solid catalysts studied during the last few years, nitrates of Li, Na, and K supported on alumina can be commonly found. Even though they present a high production of methyl esters (over 93%), they are not recognized as the best solution because the reaction is a relatively slow (over 3 hours) and present lixiviation of the active species[3].

On the other hand, Kim et al. developed a Na/NaOH/Al_2O_3 basic catalyst for the transesterification of soybean oil, which demonstrated a similar activity to that of a conventional homogeneous catalyst, NaOH[4]. Furthermore, Salinas et al. studied a potassium catalyst supported on titania for biodiesel production from canola oil[5,6], founding a very active K-based catalyst supported on a hydrothermally treated TiO_2 (20%K/TiHT), which was able to achieve full conversion in two hours of reaction[6].

In this work we studied the activity of catalysts based on different alkali metals as active species (Li, Na, and K), and using zirconia as support, for biodiesel production. The choice of ZrO_2 is due to its well-known surface chemical properties (presence of base-acid dual sites)[7], that make it a promising candidate as support. We also studied the effect of the calcination temperature of the catalysts, considering that the formation of the different active species depends on this variable, among others[6].

2. EXPERIMENTAL

2.1. Catalysts preparation

A series of M/ZrO_2 catalysts (M = Li, Na, or K) with constant metal content of 10%w/w were prepared. The ZrO_2 support was obtained by direct calcination of commercial hydrous zirconia (MEL Chemicals) at different temperatures: 500, 600 and 700 ºC for 3 hours. As result, ZrO_2 supports with three calcination temperatures were obtained. The catalysts were prepared by wet impregnation of ZrO_2 supports with each metal nitrate (Merck, p.a.). Once impregnated, the catalyst was dried in an oven at 105 ºC for 12 hours and then calcined in a muffle furnace at the same calcination temperature of the ZrO_2 used as support, i.e. for the ZrO_2 support calcined at 500 °C the catalyst was calcinated at 500 °C for 3 hours. The above procedure was the same for catalysts calcined at 600 and 700 ºC for 3 hours.

2.2. Characterization of the catalysts

The samples were characterized by N_2 adsorption, X-ray diffraction (XRD), and temperature programmed desorption of CO_2 (CO_2-TPD).

Determination of the BET specific area (Sb) of the catalysts was made by N_2 adsorption in a Micromeritics Model ASAP 2010 sorptometer. Prior to the analysis, the samples were degassed at 200 ºC.

The crystal structure of the different catalysts was studied on a Siemens D-5000 diffractometer using Cu K_α radiation and a scan rate of 0.02 degrees per minute.

Temperature programmed desorption of CO_2 experiments were made in a Quantachrome Dynamic Flow Chemisorption Analyzer ChemBet-3000 TPD/TPR instrument. Previous to the CO_2-TPD experiments, the samples were exposed to oxygen at 400°C for 1 hour, and then O_2 was change to helium maintaining the temperature (400 °C) for 30 min. After this heating treatment, the reactor was cooled to room temperature with flowing helium. Then, the samples were treated with CO_2 for 1 hour, and then CO_2 was changed to He. After flowing He, the samples were heated at a constant rate of 10 °C/min and the desorbed carbon dioxide was monitored with a thermal conductivity detector.

2.3. Catalytic activity tests

The catalytic activity in biodiesel production was measured using a batch type reactor with temperature, pressure and stirring control. The operation conditions were 60°C, 1 atm and 110 rpm. Prior to the experiments, the catalyst was dried at 110 ºC for 1 hour in an oven, in order to avoid the presence of humidity, and then 1.2 g of catalyst were loaded in the reactor. The reactor was loaded with a mixture of oil (22 mL) and methanol (29 mL), in a molar "methanol/oil" ratio of 36/1. The solid catalyst mass (1.2 g) corresponded to

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6%w/w of the total mass of the loaded mixture (20 g of oil, and 23.1 g of methanol). The methanol used (Merck) was GC grade (purity 99.9%), with less than 0.05% water. The oil used was commercial grade edible canola oil. To record the progress of the reaction, a small aliquot was analysed by mass chromatography with the following procedure: 0.5 mL sample from the reactor was injected into a vial containing 0.5 mL of 0.1 M HCl to stop the reaction. Then 0.5 mL of extracting solution was added to the same vial. The extracting solution consisted of hexane/diethylether (1/1) which contained a reference standard (eicosane, 5000 ppm). The vial was then centrifuged to separate the different phases. A small aliquot from the top phase, which contained the methyl esters, was injected into the mass chromatograph. The mass chromatograph was a GCMS-QP2010 Plus (Shimadzu) equipped with an Rtx®-5MS capillary column (Restek).

3. RESULTS AND DISCUSSION

3.1. Catalyst characterization results

3.1.1. Specific areas

The nomenclature of the catalysts prepared in this study and the corresponding specific areas (Sb) are shown in Table 1. For comparison purposes, the specific area of a non-calcined commercial hydrous zirconia was also included. As expected, the Sb of the ZrO_2 supports decreased with increasing calcination temperatures. This decrease is noticeable considering that the non-calcined commercial hydrous zirconia presents almost 400 m^2/g (382 m^2/g). For the lower calcination temperature (500 °C), the ZrO_2(500) support presents the highest decrease, with a Sb of 59 m^2/g (only 15% of the original specific area). In the case of higher calcination temperatures (600 and 700 °C), it can be observed that the Sb decreases for the ZrO_2(600) and ZrO_2(700), resulting in 45 m^2/g and 31 m^2/g, respectively.

Table 1. Nomenclature, BET specific areas (Sb), and apparent constant rates (k_{app}, obtained assuming pseudo first order in transesterification reaction) of catalysts with different alkali metals (Li, Na, K) supported on zirconia (ZrO_2), and calcined at different temperatures (500, 600 and 700 °C). The amount of CO_2 desorbed per catalyst mass (μmol/g) obtained from TPD experiments is also included.

Details	Catalyst	Sb (m^2/g)	k_{app} (h^{-1})	CO_2 desorbed (μmol/g cat)
Commercial hydrous zirconia not calcined ($Zr(OH)_4$)	ZrOH	382	-	-
$Zr(OH)_4$ calcined at 500 °C	ZrO_2(500)	59	0	N.D.
10%Li/ZrO_2 calcined at 500 °C	10Li/ZrO_2(500)	14	0.925	2491
10%Na/ZrO_2 calcined at 500 °C	10Na/ZrO_2(500)	17	1.643	2179
10%K/ZrO_2 calcined at 500 °C	10K/ZrO_2(500)	12	0.724	1975
$Zr(OH)_4$ calcined at 600 °C	ZrO_2(600)	43	0	N.D.
10%Li/ZrO_2 calcined at 600 °C	10Li/ZrO_2(600)	7	1.843	2189
10%Na/ZrO_2 calcined at 600 °C	10Na/ZrO_2(600)	11	2.771	1871
10%K/ZrO_2 calcined at 600 °C	10K/ZrO_2(600)	9	1.146	1641
$Zr(OH)_4$ calcined at 700 °C	ZrO_2(700)	31	0	N.D.
10%Li/ZrO_2 calcined at 700 °C	10Li/ZrO_2(700)	4	3.594	1625
10%Na/ZrO_2 calcined at 700 °C	10Na/ZrO_2(700)	8	4.639	1528
10%K/ZrO_2 calcined at 700 °C	10K/ZrO_2(700)	8	2.009	1383
*10%K/TiO_2 calcined at 500 °C	10K/Ti(500)	31	0.304	-
*10%K/TiNT calcined at 500 °C	10K/TiNT(500)	83	0.417	-
*20%K/TiHT calcined at 500 °C	20K/TiHT(500)	19	0.373	-
*20%K/TiHT calcined at 700 °C	20K/TiHT(700)	2	2.302	-

* Catalysts previously reported [5,6]

In the case of the ZrO_2 supported alkali-metal catalysts, Table 1 shows a decrease in the Sb, which is also observed with increasing calcination temperatures. Regarding the effect of the alkali metal type on specific area, it is not possible to find a clear correlation between the Sb values and the different catalysts. In fact, there is an approximately similar decrease of specific area with the increase in calcination temperature, except for the case of the potassium based catalyst. The latter catalyst presents only a slight decrease in specific area between calcination temperatures (12 m^2/g, 9 m^2/g, and 8 m^2/g for 10K/ZrO_2(500), 10K/ZrO_2(600) and 10K/ZrO_2(700) catalysts, respectively). The same singular behavior was also observed for the pore volume and pore diameter results (not included in Table 1),.

3.1.2. Temperature programmed desorption of CO_2

The temperature programmed desorption of CO_2 (CO_2-TPD) curves of some selected catalysts are shown in Figure 1. The quantification of desorbed CO_2 for all catalysts is included in Table 1. These values were obtained by integrating the area below the CO_2 desorption curve for each catalyst, and using a known CO_2 calibration pattern.

Figure 1A shows CO_2 desorption curves of alkali metals supported on ZrO_2 calcined at 600 °C. The curves of catalysts calcined at 500 and 700 °C were not included since they provide no additional information. When observing Figure 1A it is possible to find differences in the maximum desorption peaks of each alkali metal based catalysts. For 10K/ZrO_2(600) catalyst it can be observed a wide CO_2 desorption peak, with a maximum located approximately at 590 °C, and an amount of desorbed CO_2 of 1631 μmol per gram of catalyst (μmol/g). In the case of the $10Li/ZrO_2(600)$ catalyst, it presents a more narrow CO_2 desorption peak compared to $10K/ZrO_2(600)$ catalyst, with a maximum located around 640 °C, which is 50 °C greater than the previous one, and with the amount of desorbed CO_2 of 2189 μmol/g. The higher desorption temperature and larger amount of desorbed CO_2 obtained with this characterization technique might explain that supported alkali metal species have higher basicity and higher surface concentration of basic sites, respectively.

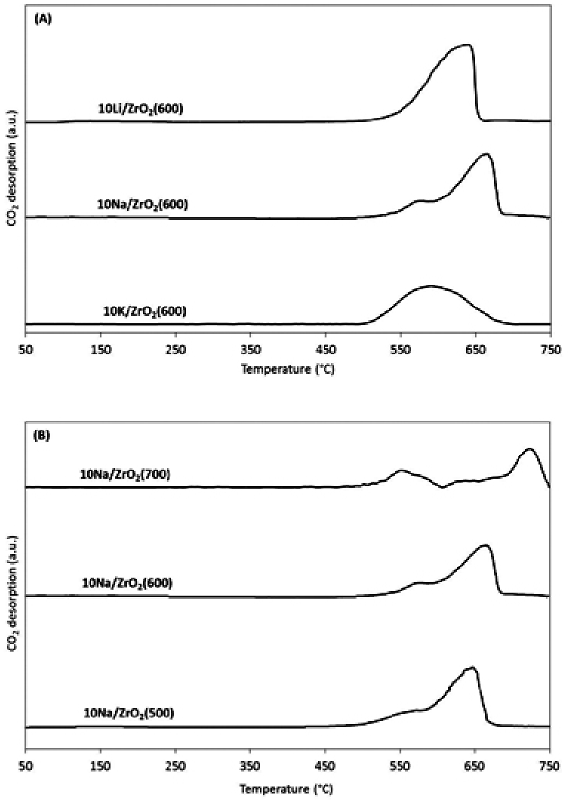

Figure 1. (A): CO_2-TPD curves of alkali metals (Li, Na, K) supported on ZrO_2 catalysts with 10%w/w constant metal loading calcined at 600 °C. (B): CO_2-TPD curves of Na/ZrO_2 catalysts with 10%w/w constant metal loading calcined at different temperatures (500, 600 and 700 °C).

Finally in Figure 1A, the CO_2 desorption curve is also shown for the $10Na/ZrO_2(600)$ catalyst, which was the only one presenting a double desorption peak, located approximately at 575 and 665 °C, and with an amount of desorbed CO_2 of 1871 μmol/g.

The analysis and conclusions obtained when comparing these alkali metals with the other two calcination temperatures (500 and 700 °C) were basically the same, and for this reason the previously stated for catalysts calcined at 600 °C is also valid for the catalysts calcined at 500 °C and 700 °C. In other words, the species of Na formed on the surface of ZrO_2 present a greater basicity when compared with the species of Li and K formed on ZrO_2, for any calcination temperature considered in this study.

Regarding that Na species present greater basicity that species of Li and K, it is interesting to observe the effect of calcination temperature of Na/ZrO_2 system, as shown in Figure 1B. The calcination temperature produces changes in the CO_2 desorption curve, as well as a decrease in the amount of desorbed CO_2. Indeed, Figure 1B shows the CO_2-TPD desorption curve for the $10Na/ZrO_2(500)$ catalyst having a shoulder and a peak whose maxima are approximately located at 560 °C and 645 °C, respectively. The calculated amount of desorbed CO_2 for this $10Na/ZrO_2(500)$ catalyst was 2179 μmol/g. When increasing the calcination temperature to 600 °C, the $10Na/ZrO_2(600)$ catalyst presents a CO_2 desorption curve similar to that of the $10Na/ZrO_2(500)$ catalyst, but shifted to a higher temperature. That is, the $10Na/ZrO_2(600)$ catalyst presents a shoulder and a peak located approximately at 575 °C and 665 °C, respectively, and with an amount of desorbed CO_2 of 1871 μmol/g. In the case of $10Na/ZrO_2(700)$ catalyst, it presents a CO_2-TPD curve with a clear double peak, whose maxima are approximately at 550 and 720 °C, and with an amount of desorbed CO_2 of 1528 μmol/g.

3.1.3. X-Ray diffraction

Considering that CO_2-TPD results indicate the importance of calcination temperatures in the formation of different alkali metal species, X-ray diffraction experiments were carried out to elucidate the crystalline character of the catalysts. The XRD results of alkali metals supported on ZrO_2 and calcined at 500, 600 and 700 °C, are shown in Figure 2A, Figure 2B and Figure 2C, respectively. Also, in each figure the main diffraction lines from patterns of compounds found in the XRD analysis were included.

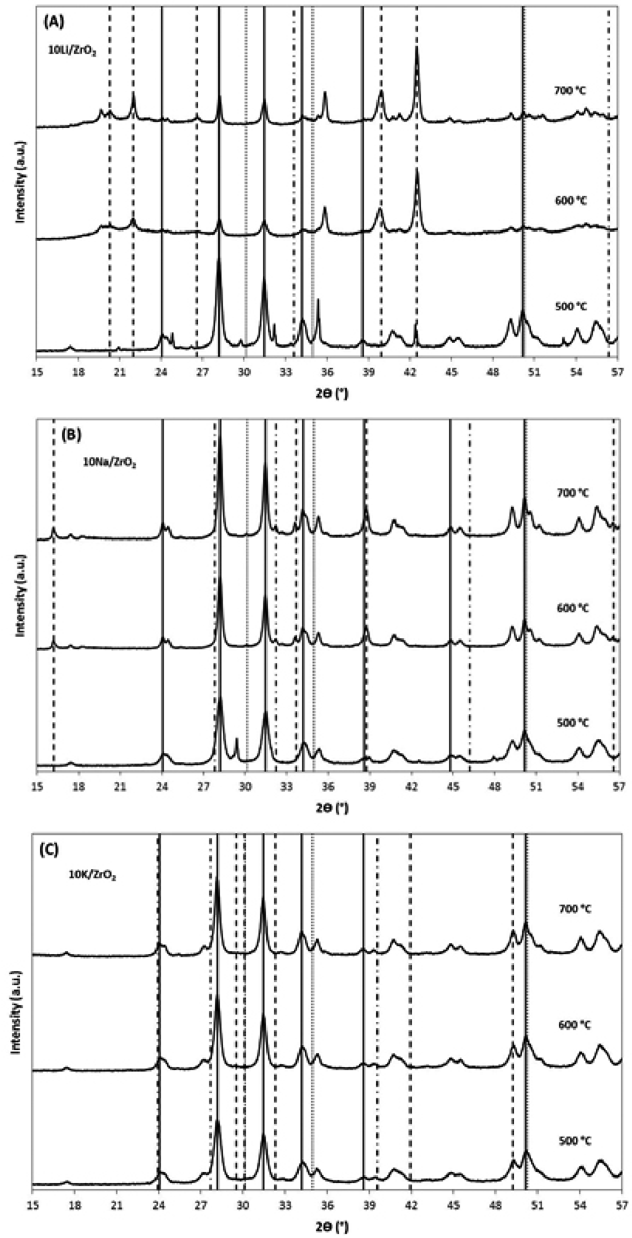

Figure 2. XRD diffractograms of alkali metals (Li, Na, K) supported on ZrO2 catalysts, with 10%w/w constant metal loading, and calcined at different temperatures (500, 600 and 700 °C). (A): Li; (B): Na; and (C): K. Main diffraction patterns lines are included for: monoclinic ZrO2 (——), tetragonal ZrO2 (·······), M2O (-·-·-·-·-), and M2ZrO3 (- - - - -), where M denotes the alkali metal (Li, Na, or K).

Figure 2A shows the diffractograms of Li/ZrO_2 catalysts calcined at different temperatures. When calcining at 500 °C, the ZrO_2 support presents a monoclinic crystalline structure (JCPDS N° 37-1484), and no diffraction peaks associated to the tetragonal phase (JCPDS N° 49-1642) can be observed. The above can be also observed at higher calcination temperatures, 600 and 700 °C, where the crystalline structure of ZrO_2 support is monoclinic, with less intense diffraction peaks compared to the calcination temperature of 500 °C. This decrease in intensity of the diffraction peaks of the monoclinic ZrO_2 might be due to higher calcination temperatures, which induces a decrease in specific area of ZrO_2 support. This smaller specific area can lead to a high concentration of surface lithium species interacting with the ZrO_2 support, and therefore reducing diffraction peaks of bare support. On the other hand, for any calcination temperature, Figure 2A do not show the presence of Li_2O species (JCPDS N° 12-0254), which could be either attributed to the formation of amorphous lithium oxide species or to the presence of dispersed Li_2O species undetectable by XRD. Nevertheless, the presence of dispersed Li_2O species is unlikely since the loading of 10%w/w lithium on the ZrO_2 support, with specific area between 14 and 4 m^2/g, is sufficient to induce the formation of crystals large enough to be detected by the XRD analysis. The most interesting result that can be observed in Figure 2A is the formation of lithium zirconate Li_2ZrO_3 (JCPDS N° 33-0843) at 600 °C. The concentration of these species increases as the temperature rises up to 700 °C as evidenced by the increase in the intensity of Li_2ZrO_3 diffraction peaks (20.3°, 22°, 26.6°, 39.9° y 42.5°). It should be noted that lithium oxide species on the 10Li/ZrO_2(500) catalyst must be in an amorphous structure because they were not detected by XRD experiments, even though they contribute to the basic character of this catalyst, which is evidenced by the highest amount of desorbed CO_2 of all the catalysts (see CO_2-TPD results). On the contrary, lithium zirconate species are clearly observed in the 10Li/ZrO_2(600) and 10Li/ZrO_2(700) catalysts, which have a greater basicity than the species formed at lower temperatures (500 °C). The latter is consistent with the CO_2-TPD results for those catalysts. Moreover, the XRD spectrum of the 10Li/ZrO_2(700) catalyst shows the most intense diffraction peaks of Li_2ZrO_3 species, which is consistent with the CO_2-TPD results. Those results show a maximum CO_2 desorption at higher temperature, which is associated with a large basicity.

A similar analysis was carried out for the ZrO_2 supported Na catalysts calcined at different temperatures. The results showed the appearance of sodium zirconate species, Na_2ZrO_3 (JCPDS N° 35-0770), on the Na/ZrO_2 catalyst calcined at 600 °C. The intensity of such signal slightly increased when calcining at higher temperature as shown by the 10Na/ZrO_2(700) catalyst. The analysis of the Na/ZrO_2 catalysts did not showed the formation of Na_2O species (JCPDS N° 23-0528) at any calcination temperatures, which is likely explained by the same reasons as pointed out for the 10Li/ZrO_2(500) catalyst.

In the case of the K/ZrO_2 catalysts, Figure 2C, it can be observed in that the XRD results of the samples at different calcination temperatures, (10K/ZrO_2(500), 10K/ZrO_2(600), and 10K/ZrO_2(700)), did not show the formation of K_2ZrO_3 species (JCPDS N° 72-0824), and neither K_2O species (JCPDS N° 47-1701).

3.2. Biodiesel production

The results of the catalytic activity study for biodiesel production are shown in Figure 3, specifically the effect of the alkali metal type and calcination temperature.

Figure 3A shows the catalytic activity curves based on the three alkali metals (Li, Na, and K) and calcined at 500 °C. As a reference, the result of bare ZrO_2(500) support was included, although it did not present any activity, which rule out the possible contribution of the support to the activity of the catalyst. It was found that the activity of these catalysts calcined at 500 °C can be ordered in the following sequence: Na > Li > K. It is remarkable that the 10Na/ZrO_2(500) catalyst reaches complete conversion after 2 hours of reaction, which makes it a good candidate for a heterogeneous catalyst.

As the calcination temperature rises up to 600 °C, an increase in biodiesel production is observed for all catalysts, as shown in Figure 3B. Similar to the case of the samples calcined at 500 °C, the catalytic activity sequence was relatively the same: 10Na/ZrO_2(600) ≈ 10Li/ZrO_2(600) > 10K/ZrO_2(600). Accordingly, the rise of calcination temperature produces an increase in the activity of all catalysts, although at this temperature (600 °C) the Na and Li catalysts are similar. It is interesting to note that the latter catalysts reach complete conversion within 1 to 1.5 hours of reaction, which suggests that the increase in calcination temperature is favourable for on ZrO_2 systems. Additionally it should be noted that the bare ZrO_2(600) support did not present any catalytic activity.

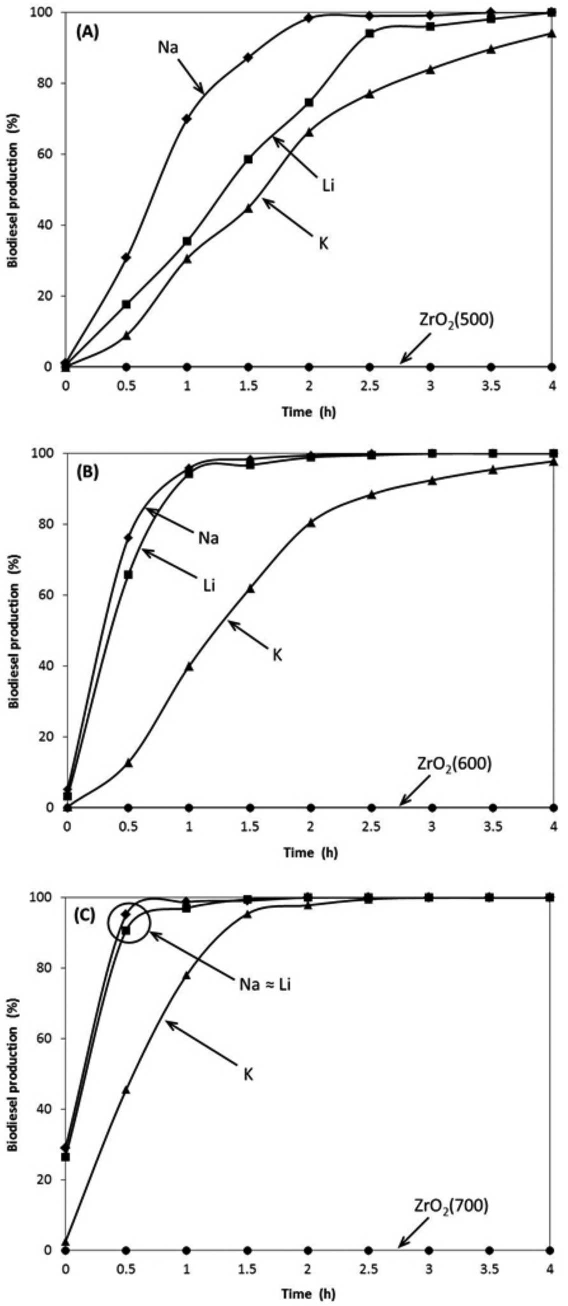

Figure 3. Conversion to methyl esters with reaction time of alkali metals (Li, Na, K) supported on ZrO2catalysts, with 10%w/w constant metal loading and calcined at different temperatures: (A): 500°C; (B): 600°C; and (C): 700 °C. Alkali metals in figure are: Li (n), Na (¨), and K (▲). ZrO2 support (•) with different calcination temperatures does not show activity.

Similar conclusions can be obtained when the catalysts are calcined at 700 °C, Figure 3C, where it can be observed that this higher calcination temperature produces once again an increase in the activities of all catalysts. The observed sequence of activity was maintained: 10Na/ZrO_2(700) ≈ 10Li/ZrO_2(700) > 10K/ZrO_2(700). In fact, both Na and Li based catalysts present basically the same activity curves in the production of biodiesel with full conversion within 0.5 to 1 hour. In the same way that the previous temperatures, the 10K/ZrO_2(700) catalyst was the least active, whereas the bare ZrO_2(700) support did not present any catalytic activity.

According to that reported in literature and previous works by our group[5,6], whose studies were carried out under the same experimental reaction conditions used here, it can be assumed a pseudo-first order reaction for the transesterification reaction.

Considering this assumption, the apparent rate constants (k_{app}) for the catalysts were obtained, whose estimated values are shown in Table 1. In agreement with the results shown in Figure 3, it is observed that there is a sequence of activity for the catalysts calcined at 500 °C, in terms of the type of alkali metal: Na > Li > K (1.643 > 0.925 > 0.724 h^{-1}, respectively). It is also possible to observe that for any alkali metal, higher calcination temperature produces an increase in the value of k_{app} (e.g. for the sodium based catalysts: $10Na/ZrO_2(700)$ > $10Na/ZrO_2(600)$ > $10Na/ZrO_2(500)$, i.e., 4.639 > 2.771 > 1.643 h^{-1}, respectively). The only difference respect to that shown in the activity curves (Figure 3), is that according to the estimated values of k_{app}, the sequence of activity of the alkali metals in this study was independent of the calcination temperature and it followed the order: Na > Li > K.

It should be mentioned that the catalysts supported on ZrO_2 in this study have higher activities than those reported previously by our group, where TiO_2 was used as support[5,6]. Table 1 shows the values of the apparent rate constants of the best catalysts using TiO_2 as support, including hydrothermally treated TiO_2 supports (denoted as TiNT and TiHT). It is observed that for any calcination temperature, the k_{app} of the ZrO_2 based catalysts were larger than the k_{app} of the 10K/Ti(500), 10K/TiNT(500) and 20K/TiHT(500) catalysts. The best catalyst of the series with TiO_2 as support, 20K/TiHT(700), presented a considerably high value of k_{app} [6]. However this value is in the range of what was estimated for the $10K/ZrO_2(700)$ catalyst, not even considering that the loading of K was half in the latter catalyst. The most active catalysts of the present study are the $10Li/ZrO_2(700)$ and $10Na/ZrO_2(700)$ catalysts, which present k_{app} values high above the k_{app} value of the 20K/TiHT(700) catalyst, as can be observed in Table 1.

Regarding the specific areas of the catalysts and their relation with the respective activities in biodiesel production, it can be noted that there is no direct or proportional correlation between these two variables. On the contrary, the highest activities (considering k_{app}) of the catalysts supported on ZrO_2 were obtained with those catalysts calcined at high temperatures, or in other words, lower specific areas. As regularly occurs in catalysis, the higher specific areas favor the dispersion of active species on the support. Nevertheless, the results shown in this work do not follow this trend. Although uncommon, this unexpected result was also observed in a previous work[6], where TiO_2 was used as support and the best catalyst was the one subjected to the higher calcination temperature (having the lower specific area). In this regard, a similar example is shown in Table 1 (20K/TiHT(700) > 20K/TiHT(500)).

Considering the CO_2-TPD results, it is important to remember that the $10Li/ZrO_2(600)$ catalyst presents a more narrow and larger CO_2 desorption peak compared to the $10K/ZrO_2(600)$ catalyst, with a maximum located around 640 °C (see Figure 1A). Also, the high amount of CO_2 desorption (2189 μmol/g) from the $10Li/ZrO_2(600)$ catalyst, explains the higher activity of $10Li/ZrO_2(600)$ compare to that of $10K/ZrO_2(600)$. In other words, the higher desorption temperature and larger amount of desorbed CO_2, evidence a greater basicity and higher surface concentration of basic sites on the $10Li/ZrO_2(600)$ catalyst..

On the other hand, the $10Na/ZrO_2(600)$ catalyst is the most active when calcining at 600 °C (k_{app} = 2.711 h^{-1}). The reason for this enhanced activity in relation to that obtained with the $10Li/ZrO_2(600)$ catalyst (k_{app} = 1.843 h^{-1}) can be explained by the higher basicity of Na species formed on ZrO_2. The $10Na/ZrO_2(600)$ catalyst presents a higher desorption temperature (over 25 °C of difference), although the amount of desorbed CO_2 is lower compared with the $10Li/ZrO_2(600)$ catalyst (1871<2189 μmol/g). Based on these differences, we suggest that the desorption temperature has a relatively greater influence than the amount of CO_2 desorbed, thus explaining the higher activity of the $10Na/ZrO_2(600)$ catalyst over the $10Li/ZrO_2(600)$ and $10K/ZrO_2(600)$ catalysts.

When comparing the CO_2-TPD results of the $10Na/ZrO_2(500)$ and $10Na/ZrO_2(600)$ catalysts (see Figure 1B), the $10Na/ZrO_2(600)$ catalyst presents a greater k_{app} than $10Na/ZrO_2(500)$ (2.771 > 1.643 h^{-1}), due to the fact that the Na species formed in $10Na/ZrO_2(600)$ catalyst present a greater basicity (higher desorption temperature). Increasing the calcination temperature produces a decrease of the amount of desorbed CO_2 (from 500 to 600 °C, drops from 2179 down to 1871 μmol/g). Despite the decrease of the amount of desorbed CO_2, i.e. decrease of the concentration of basic sites on the surface of $10Na/ZrO_2(700)$, it can be noted that the Na species formed on ZrO_2 show a desorption peak at the higher temperature (720 °C), which might be the responsible of the high activity of this catalyst, having also the highest k_{app} from the Na/ZrO_2 system and from all the catalysts prepared in this study (4.639 h^{-1}).

The analysis of the CO_2-TPD results suggests that the greater activity in the production of biodiesel can be attributed to the existence of alkali metal species that require a high desorption temperature with an adequate amount of desorbed CO_2. These two variables (temperature and amount or desorbed CO_2) depend on the type of alkali metal selected to be supported on ZrO_2, and on the calcination temperature. As discussed above, the specific areas of the best catalysts are rather low due to the high calcination temperatures used. This thermal treatment not only induces a decrease of the specific area, but also decreases the amount of desorbed CO_2. Although high specific areas are important to favor a greater concentration of alkali metal species distributed on the surface (higher adsorption of CO_2), there is no guarantee that the catalyst will have the highest activity. Instead, a high calcination temperature is responsible for the formation of highly active alkali metals species, as was reported previously in another study[7]. This explains the high activity of the catalysts calcined at high temperature ($10Na/ZrO_2(700)$), which was likely related to highly active species but not in a large enough amount to show a significant CO_2 desorption. Future studies aim at making use of a hydrothermally treated ZrO_2 support, denominated as “refluxed zirconia” in previous work of our research group. This hydrothermal treatment is applied to achieve a thermal stabilization of ZrO_2 and further obtain greater specific areas at high calcination temperatures[14].

The analysis of XRD results is very important for complementing the above discussion with the CO_2-TPD results. The lithium oxide phase on the $10Li/ZrO_2(500)$ catalyst was not detected by XRD analysis (Figure 2A), but the highest amount of desorbed CO_2 was observed on this catalysts. In addition, considering that the $10Li/ZrO_2(500)$ catalyst presented a significant activity (k_{app} = 0.925 h^{-1}) and that the $ZrO_2(500)$ support had no activity in biodiesel production, then it can be concluded that lithium oxide species formed a highly active amorphous structure on the catalyst surface. Furthermore, the $10Li/ZrO_2(600)$ and $10Li/ZrO_2(700)$ catalysts clearly showed the presence of lithium zirconate species, which led to greater activity than the species formed at lower temperatures (500 °C) (see k_{app} in Table 1). Moreover, the XRD diffractogram of the $10Li/ZrO_2(700)$ catalyst (Figure 2A) shows the most intensity diffraction peaks related to Li_2ZrO_3 species, which correlates with the CO_2-TPD results of this catalyst. It shows a maximum of CO_2 desorption at higher temperature, i.e. species with higher basicity and therefore related to higher activity on the $10Li/ZrO_2(700)$ catalyst. In the same way, the high activity in biodiesel production of the $10Na/ZrO_2(600)$ and $10Na/ZrO_2(700)$ catalysts would be attributed to the formation of Na_2ZrO_3 species, which are more active than sodium oxide species formed at lower temperatures (500 °C). The CO_2 desorption curves for the $10Na/ZrO_2(600)$ and $10Na/ZrO_2(700)$ catalysts (see Figure 1B) show that these Na_2ZrO_3 species have high basicity, even higher when the calcination temperature increases (the same as with the Li/ZrO_2 system). Also when Li and Na were supported on ZrO_2, these alkali metal zirconate species were formed. In the case of the Na/ZrO_2 catalysts, the zirconate species present greater basicity, as can be observed in Figure 1A.

As before, the use of XRD and CO_2-TPD results can help to explain why the K/ZrO_2 catalysts were the less active in biodiesel production among the three alkali metals studied. The XRD analysis showed that no potassium zirconate species were formed and only amorphous potassium oxide species were obtained (undetectable by XRD, see Figure 2C). The latter species present less basicity (lower CO_2 desorption temperature, see Figure 1A) and lower concentration of surface species (lower amount of CO_2 desorbed, see Table 1), compared to the Li/ZrO_2 and Na/ZrO_2 catalysts at same calcination temperature.

It is important to note that, in accordance with the XRD results, the formation of lithium and sodium zirconates were also reported in some other works, used as CO_2 absorbents[8,9] and as catalysts for biodiesel production[10-12]. However, further studies are required to completely assure the formation of M_2ZrO_3 species, such as for example using an Electrophoretic Migration technique.

For comparison purpose and considering only studies that have similar reaction parameters as those used in this work, reported reaction times to achieve complete conversion vary between 1 and 3 hours[5,6,10-12]. On the other hand, the 10%w/w Na supported on ZrO_2 and calcined at 700 °C catalyst, reported in this study, is able to achieve complete conversion in just 30 minutes. Some factors of this difference in the activity is that the preparation conditions and the nature of precursors or active species to be supported, can influence the physicochemical properties of the final catalyst, such as porosity, specific area, shapes and particle sizes of zirconia[13] (among others), and these changes can effect in the final catalytic activity.

In summary, it can be concluded that the ZrO_2 support allows generating high active catalysts for the production of biodiesel. This result would confirm the initial hypothesis of using ZrO_2 as support, considering its known surface chemical properties. The use of ZrO_2 as support of alkali metals represents an interesting alternative for the preparation of solid catalysts used in the heterogeneous production of biodiesel. The formation of different species depends on the type of alkali metal, with sodium presenting the highest activity in this study. Besides the increase in the calcination temperature, which leads to a decrease of the specific area, the thermal treatment promotes the formation of alkali metal zirconate species (using Li or Na), which are highly active for the transesterification reaction. This higher activity is due to the strong basic nature of the alkali metal zirconates. In a following study of our research group, we propose to optimize the Na/ZrO_2 system, which presented the highest activity in this work, considering the effect of the metal loading and reusability among other variables. In summary, the Na/ZrO_2 catalyst constitutes a real alternative to produce biodiesel through a heterogeneous and continuous process.

4. CONCLUSIONS

The results presented in this study allowed us to demonstrate that ZrO_2 is a support that presents good surface properties to be used in the preparation of catalysts based on alkali metals for heterogeneous biodiesel production. Within the studied alkali metals, the following sequence of catalytic activity has been found in decreasing order: Na > Li > K. Although the increase in the calcination temperature produces an increase in the activity of all catalysts, the previous sequence remains unchanged regarding this variable. The results of characterization would explain the greater activity of the Na/ZrO_2 system, which might be due to the appearance of sodium zirconate (Na_2ZrO_3) species in the structure of the catalyst. These sodium zirconates species were formed during the calcination at high temperatures. The alkali metal zirconate species were formed in Li and Na containing catalysts and they were attributed to the high basic character of the catalysts. The basicity was higher for the case of the Na/ZrO_2 catalyst. It is proposed that formation of Na_2ZrO_3 species is responsible for the highest activity of Na supported on ZrO_2, reaching complete conversion in less than one hour of reaction.

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