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Improvement on the Catalytic Performance of Mg–Zr Mixed Oxides for Furfural–Acetone Aldol Condensation by Supporting on Mesoporous Carbons

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A new procedure for improving the performance of the most common catalysts used in aqueous-phase aldol condensation (Mg–Zr mixed oxides) reactions is presented. This reaction is of interest for upgrading carbohydrate feedstocks. The procedure involves supporting Mg–Zr oxides on non-microporous carbonaceous materials, such as carbon nanofibers (CNFs) or high-surface-area graphites (HSAGs), using either incipient wetness or coprecipitation procedures. The use of HSAGs together with the coprecipitation method provides the best performance. Results obtained for the cross-condensation of acetone and furfural at 323 K reveal that the catalyst performance is greatly improved compared to the bulk oxides (96.5% conversion vs. 81.4% with the bulk oxide; 87.8% selectivity for C_{13} and C_8 adducts vs. 76.2% with the bulk oxide). This difference is even

Introduction

Processes based on using biomass as a raw material for the synthesis of fuels and chemicals are considered among the most promising technologies for the mitigation of fossil-fuel dependency.^[1,2] The main difficulty for transforming biomass into biofuels is that it relies on the differences in their molecular composition: biofuels are hydrophobic whereas carbohydrates are hydrophilic and have high oxygen/carbon ratios.^[3] Therefore, new technologies are required for obtaining biofuels from this raw material.^[3-5] The main alternative consists of low-temperature acid hydrolysis of wooden feedstocks,^[6] a process in which the formation of sugar derivatives (furfural, hydroxymethylfurfural, etc.) is catalyzed by homogeneous or heterogeneous acids.^[7] These products can be used as biofuels precursors; however, their short carbon-chain lengths prevents their use as diesel fuel precursor, and their non-branched character leads (upon hydrogenation) to poor quality gasoline

The formation of C–C bonds between precursor molecules leads to C_8 – C_{15} adducts, which are platform molecules for diesel-fuel synthesis. One approach for obtaining these larger *n*-alkanes involves the aldol condensation of aldehydes or ketones to form C_8 and C_{13} adducts, which can yield the desired alkanes after hydrogenation and deoxygenation reactions,^[8–10] as depicted in Scheme 1.

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Fax: (+ 34) 985103434 more prominent in terms of rates per catalytically active basic site (four and seven times greater for C_8 and C_{13} adducts, respectively). The improved performance is explained in terms of a more appropriate basic site distribution and by greater interaction of the reactants with the carbon surface. In addition, deactivation behavior of the catalyst is improved by tuning the morphology of the carbonaceous support. An important enhancement of the catalytic stability can be obtained selecting a HSAG with an appropriate pore diameter. With HSAG100 the activity decreased by less than 20% between successive reaction cycles and the selectivity for the condensation products remained almost unaltered. The decrease is greater than 80% for the bulk oxides tested at these conditions, with important increases in the selectivity for by-product formation.



Scheme 1. Formation of C_8 and C_{13} alkenes by aldol condensation of furfural and acetone, followed by hydrogenation-dehydration reactions.

Different heterogeneous catalysts have been studied either in the aqueous or in the gas phase,[11-13] showing that the concentration of basic sites and the distribution of basicity strength are key parameters in C-C bond formation reactions.^[8] We recently reported the study of furfural and acetone aldol cross-condensation using Mg-Zr, Mg-Al, and Ca-Zr catalysts. High selectivities for both biofuel precursors were obtained and the Mg-Zr catalyst showed the highest activity (61.5% of C_{13} final selectivity) with more than 85% of furfural conversion and low reactants losses from side reactions or solid-deposit formation.^[14] Activity results were compared to the surface properties of the tested mixed oxides, showing that the formation of C_8 and C_{13} adducts are catalyzed by medium-strength basic sites, whereas the most basic sites lead to the formation of heavy side-products. Analysis of the coke deposits revealed that there was a high contribution of the C13 adduct, its low solubility favoring deposition onto the surface, blocking the basic sites, and limiting the reaction evolution. This disadvantage can be solved by integrating condensation and partial hydrogenation into one single step. For this purpose, the mixed oxide must be impregnated with palladium. Bi-functional catalysts (Pd/Mg–Zr, Pd/Mg–Al and Pd/Ca–Zr) were studied and the best results were reached with Pd/Mg–Zr in the presence of $H_2^{.[15]}$

The reaction was catalyzed by medium-strength basic sites; therefore, strategies for increasing the concentration of basic sites led to higher condensation rates. Dispersion of the mixed oxides onto an inert support led to the presence of structural defects creating new basic sites, as reported by Winter et al. for the dispersion of hydrotalcites onto carbon nanofibers.^[16,17] However, there are several points to note: firstly, most of the inorganic supports have a distribution of acidic/basic sites that can interfere with the corresponding active phase and catalyze undesired side reactions. Secondly, activated carbons are not appropriate because of their microporous character, hindering both the homogeneous dispersion of the active phase and the diffusion of the reactants in the porous structure. Thus, graphitic supports, such as carbon nanotubes (CNTs), have good properties for the dispersion of active phases without altering the chemical behavior or introducing mass-transfer effects.^[18] The main disadvantages of these materials are their low surface area (same order of magnitude as the geometric area^[19]) and the low concentration of anchoring sites for active-phase dispersion.

Other carbon materials such as high-surface-area graphites (HSAGs) can be considered as an alternative support. HSAGs are prepared by the mechanical modification of synthetic graphites. This leads to disordered graphitic layers, resulting in marked mesoporous character and moderate surface areas $(100-500 \text{ m}^2 \text{g}^{-1})$. To the best of our knowledge, these materials have not been previously used as supports for this type of catalyst, despite their interesting properties. Furthermore, the unsaturated valences at the edges of the graphitic layers lead to the formation of oxygenated functional groups, which act as anchoring sites during the active-phase addition.^[20]

We report in this article a study of the improvement of the catalytic performance of a Mg–Zr mixed oxide for the furfural–acetone aldol condensation by supporting this active phase on carbon nanofibers (CNFs) and HSAGs with different surface

areas. This study includes the role of the preparation procedure, the correlation of activity trends with the physicochemical characterization of the materials, and the determination of the deactivation behavior of the catalysts.

Results and Discussion

Characterization

The main morphological properties of the studied catalysts are shown in Table 1. The adsorption-desorption isotherms obtained in all cases are type IV (BDDT Classification) and show the characteristic pattern for mesoporous solids. The data obtained were consistent with that expected, showing an increase in the surface area for those materials in which the original surface area was low (CNFs and HSAG100), which was caused by a swelling of the original structures upon dispersion of the active phase.^[21] Supports with the highest surface area (HSAG300 and HSAG500) presented a decrease in their surface area after impregnation with the mixed oxides, because of the partial blockage of the pore structure. Supported catalysts showed an increase in the pore diameter, which is related to Mg-Zr deposited onto the surface blocking the smaller pores of the carbon material. Pore volumes show slight variations, attributed to modifications of the morphology of the supports during the preparation process.

Catalyst crystallography was evaluated by XRD analysis; diffraction patterns are given in Figure 1. These patterns are characterized by the presence of a peak at $2\theta = 26^{\circ}$ (not shown), characteristic of a highly graphitic carbon structure (002), with similar intensity in all cases. A crystallinity loss (peak widening) is observed when the mixed oxide is supported on the carbonaceous material, in good agreement with its decrease in crystal size. This was also seen in other works with similar carbon materials.^[13] Comparing the diffractograms for the HSAG-based catalysts, Mg-Zr/HSAG300* (the only catalyst prepared by using incipient wetness impregnation) showed the maximum loss, whereas catalysts prepared by coprecipitation retained the crystallographic structure of the parent oxide. The CNFbased catalyst loses almost all of the crystallinity of the parent mixed oxide, although the catalyst was prepared by coprecipitation. In general, there was not significant displacement be-

Table 1. Morphological (nitrogen physisorption) and acid-base properties of the catalysts and supports used in this work.									
Catalyst	Morphologi S [m²g ⁻¹]	rphological properties $n^2 g^{-1}$] $D_p [Å] V_p [cm^3 g^{-1}]$		Basic sites [mmol g ⁻¹], (CO ₂ -TPD, [K]) bicarb. bident. monodent.			Acidic sites [mmol g ⁻¹], (NH ₃ -TPD, [K]) weak medium strong		
Mg-Zr	78	342	0.8	-	120 (427)	13 (585)	62 (425)	239 (550)	158 (863)
HSAG100	107	107	0.26	0.02(377)	-	-			
MgZr/HSAG100	110	167	0.49	11 (400)	5.5 (513)	32 (776)	117 (411)	-	85 (943)
HSAG300	321	58	0.47	0.01 (398)	-	-			
MgZr/HSAG300*	270	83	0.47	19 (386)	-	19 (716)	448 (410)	-	-
MgZr/HSAG300	243	80	0.39	10 (394)	17 (506)	19 (841)	984 (389)	-	85 (927)
HSAG500	580	75	0.75	-	0.1 (432)	-			
MgZr/HSAG500	337	79	0.61	10 (338)	13 (453)	20 (730)	489 (425)	-	24 (923)
CNF	32	160	0.17						
MgZr/CNF	41	184	0.20	2.1 (369)	1.6 (466)	38 (702)	12 (475)	197 (595)	114 (984)

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Figure 1. XRD diffractograms of the fresh catalysts used: (a) Mg–Zr; (b) Mg– Zr/HSAG100; (c) Mg–Zr/HSAG300*; (d) Mg–Zr/HSAG300; (e) Mg–Zr/HSAG500; (f) Mg–Zr/CNF. Marked peaks correspond to periclase phases.

tween the phases analyzed in the bulk material and those obtained in the supported materials; however, there was a slight shift to lower diffraction angles observed. The main peaks related to the mixed oxide are those associated with periclase (MgO), located at $2\theta = 37^{\circ}$, 43° , 62° , and 78° .^[22] The peak located at $2\theta = 43^{\circ}$ could also be associated to (101) graphene layers. However, the proportionality between peaks at $2\theta =$ 43° , 62° , and 78° was the same as in the bulk material; therefore this peak was also attributed to periclase. Crystalline phases related to tetragonal ZrO2 were detected with only small peaks at $2\theta = 30^{\circ}$ in Mg–Zr/HSAG100 and Mg–Zr/ HSAG500; therefore, this metal was more affected by the impregnation method and is present mainly as an amorphous phase. No phases related to the mixed oxide were found. This was previously observed in other works with Mg-Zr in which only periclase and low-intensity peaks of tetragonal zirconia are observed.^[23] Only in the work of Sádaba et al.^[24] is the presence of a mixed oxide reported. However, these authors state that the peaks are only observed at Mg/Zr ratios lower than 2.5, whereas this ratio in our study was greater than four.

Mixed oxide particle sizes and dispersions were studied by TEM and the micrographs are shown in Figure 2. In micrographs corresponding to Mg–Zr/HSAG100, Mg–Zr/HSAG300, and Mg–Zr/HSAG500, the particles present a regular hemispherical geometry and the crystallite sizes have been determined by counting 100 particles of different micrographs (histograms are also depicted in Figure 2). The average crystallite diameters are shown in Table 2. Micrographs of Mg–Zr/ HSAG300* and Mg–Zr/CNF display irregular deposits of mixed oxides on the supports and the crystallite size could not be ac-



Figure 2. TEM micrographs: (a) Mg–Zr/HSAG100; (b) Mg–Zr/HSAG300*; (c) Mg–Zr/HSAG300; (d) Mg–Zr/HSAG500, and (e) Mg–Zr/CNF.

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Table 2. Particle size (TEM), XPS O 1s binding energy (B.E.), surface composition, and bulk metal loadings (ICP-OES) for the catalysts used in this work.

Catalyst	TEM Dc	XPS O 1s	XPS supe	rficial compos	ICP-OES results	
	[nm]	B.E. [eV]	Mg	Zr	Mg/Zr	Mg/Zr
Mg-Zr	-	529.0	41.9	3.9	10.7	4.4
MgZr/HSAG100	12	530.1	37.8	3.1	12.7	5.1
MgZr/HSAG300*	-	530.6	16.5	1.0	16.5	4.0
MgZr/HSAG300	11	529.6	38.2	3.6	10.6	4.5
MgZr/HSAG500	8	530.1	42.0	3.0	14.0	5.3
MgZr/CNF	-	532.0	14.0	8.0	1.8	0.34

curately estimated. Mg–Zr/CNF micrographs were similar to those reported by Winter et al,^[16] these results were consistent with XRD results, showing that incipient wetness impregnation is not a good method for supporting these oxides. The results also showed that the use of HSAGs as supports led to more crystalline and dispersed particles in the active phase compared to the use of CNFs.

SEM was used to analyze the surface morphology and to confirm the homogeneous dispersion of Mg and Zr over all of the carbon surfaces. The micrographs obtained (not shown here) revealed that the supported materials maintained the morphological aspect of the pattern supports, as previously reported.^[19] The CNF material revealed a fibrous morphology with the mixed oxide particles deposited over it, whereas the HSAG supports showed a granular and spongy appearance, with the mixed oxides more homogeneously dispersed. The surface composition was analyzed by using energy dispersive X-ray (EDX) spectroscopy. Five different and random points were chosen to evaluate the atomic disposition of Mg and Zr. It was concluded that in all of the supported materials, Mg and Zr were present as mixed oxides, without segregation between both oxides. Consequently, the supported materials have the same active phases as the bulk material and their catalytic activities could be compared with the unsupported mixed oxide.

Chemical analysis of the surface composition was performed by using X-ray photoelectron spectroscopy (XPS) and the bulk composition was analyzed by using inductively coupled plasma optical emission spectroscopy (ICP–OES), after leaching of the samples in a hydrochloric–nitric acid mixture (1:30). As ICP–OES relies on the efficiency of the leaching of the solid, only accurate data for Mg/Zr ratio could be obtained. The concentration of Mg and Zr at the catalyst surface, as well as the Mg/Zr ratios in the surface and in the bulk material, are reported in Table 2. In addition, XPS analysis of the samples revealed the presence of Na in very low quantities (<1%), as a residue from NaOH used in the preparation process.

Homogeneous behavior has been observed for the three catalysts prepared by coprecipitation using different HSAGs as supports. However, in the case of the catalyst prepared by incipient wetness impregnation (Mg–Zr/HSAG300*) and the catalyst prepared using CNFs as the support, the behavior is clearly different. For Mg–Zr/HSAG300*, Mg and Zr concentrations are markedly lower but retain the stoichiometric ratio. This low

value is justified when considering the low solubility of the zirconium precursor that limits the amount of mixed oxide that can be synthesized by using the dryimpregnation method. For the nanofibers, in addition to the low concentration of both species, the Mg/Zr ratio is completely different to the expected ratio, suggesting a preferential adsorption of the zirconium precursor onto the carbon surface. This is

not only related to the concentration of anchoring sites (expected to be lower in the case of CNFs), but also to the electrostatic interactions of the ionic precursors with the surface. Thus, the zero-point charge (ZPC) for the HSAG is between 3 and 3.5, whereas it is higher than 5 for the CNFs. As the pH value of the precursor solution is approximately 6.4 and ZrO²⁺ is a more voluminous cation than Mg²⁺, this led to a higher Zr surface concentration observed for CNFs. Comparison of XPS and ICP–OES results showed a significant surface increase of the Mg concentration, which can justify the subsequent modification of the basic properties.

XPS analysis was also used to qualitatively evaluate the basicity of the materials, as the position of the O1s peak provides insight into the basicity of crystalline solids; higher binding energies suggest lower basic strengths.^[25] The values of the O1s binding energy are summarized in Table 2. Comparing these results with the value obtained for Mg-Zr (529.0 eV), the basic sites of the bulk materials are stronger than the corresponding supported catalysts; Mg-Zr/HSAG300 is the most similar in terms of the global basicity. Concerning the deconvolution of the O1s peaks (not presented here), only the bulk material presents different types of contributions, with a very intense peak at 529.1 eV from the O²⁻ species in MgO^[26] and a less intense signal at 532.2 eV, corresponding to the presence of hydroxyl groups on the surface of MgO and/or ZrO₂.^[27] The supported materials only show one peak, corresponding to the strongest groups. These results were checked by using CO2temperature-programmed desorption (CO₂-TPD) analysis.

CO2-TPD results are detailed in Table 1, expressed as concentration and strength distribution of the basic centers on the surface. The original graphites and nanofibers were treated by using the same temperature program as that of the supported materials, with a maximum over 850 K. With this treatment, the CO₂ signal from carbon pyrolysis could be discarded. The analysis of the bulk mixed oxide is also shown. Mg-Zr showed the highest concentration of basic sites (133.4 μ mol g⁻¹), distributed as both bidentate and monodentate sites. All of the supported catalysts showed, in addition to bidentate and monodentate centers, weaker sites assimilated to bicarbonates. Analyzing the global results, all of the supported materials had similar basicity, with values between 38 (Mg–Zr/HSAG300*) and 48 μ mol g⁻¹ (Mg–Zr/HSAG100). However, the strength distribution obtained for Mg-Zr/CNF was very different, that is mainly monodentate centers, whereas the

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graphitic materials had a more homogeneous distribution among weak, medium, and strong basic sites. Basicity data obtained were in good agreement with binding-energy values obtained by XPS.

The acidity of the catalysts was analyzed in terms of concentration and strength distribution of the acidic sites by using NH₃-TPD; the data obtained are detailed in Table 1. The relationship between the temperature of the desorption peaks and the type of acidity was obtained by using the method proposed by Arena and co-workers: desorption peaks with a maximum in the ranges 453-523, 553-603, and 653-773 K are currently attributed to NH₃ chemisorbed on weak, medium, and strong acid sites, respectively. It is not possible to discriminate between Brønsted and Lewis acidity.^[28] Supported catalysts had a desorption peak at temperatures over 800 K, not present in the bulk material, that was associated with functional groups of the graphite and nanofiber supports.^[29] These peaks, which are associated to carbonaceous supports are not taken into account in the general discussion as it was concluded in previous work that the acidic sites that influence the reaction are of weak and medium strength.^[14] The acidity of the catalysts supported on graphite showed similar trends, with different concentrations but similar strength distribution. In all of these materials medium-strength acidic sites disappeared, but their contribution to the global acidity for the bulk material and the CNFs is important. The weakest acidity increased in supported materials, mainly in Mg-Zr/HSAG300.

Catalytic activity

Aqueous phase aldol condensation of acetone and furfural was previously performed at 323 K over the bulk Mg–Zr oxide, after 24 h reaction time selectivities of 61.5 (C_{13}) and 14.7% (C_8) were obtained with a carbon balance closure of 98.4%.^[14] As previously mentioned, the surface chemistry of mixed oxides (especially basic site distribution) largely changes after deposition onto a carbonaceous support. As aldol condensation reactions are catalyzed by basic sites, catalytic activities are expected to change accordingly. To study this, CNFs and HSAGs (taking HSAG300 as representative) were tested as supports for the active phase for the formation of C_8 and C_{13} at 323 K. The final results (after 24 h reaction time) are shown in Figure 3. Selectivities are defined as carbon atoms in each considered product (C_8 or C_{13}) divided by acetone and furfural atoms in the feedstock.

When comparing reactant conversions and products selectivities, it was observed that catalysts with poor active-phase dispersions (Mg–Zr/HSAG300* and Mg–Zr/CNF) only yield the C_8 adduct, but never more than 10%, with negligible production of the C_{13} adduct. In contrast, the Mg–Zr/HSAG300 catalyst yielded higher reactant conversions and C_8 selectivity compared to the bulk oxide (the C_{13} selectivity and the carbon balance closure are very similar). The lower concentration of the active phase (in all the cases, 0.5 g of catalyst were used) suggested that this type of catalyst presents enhanced activity compared to the bulk oxides.



Figure 3. Activity results obtained after 24 h for the aldol condensation of furfural and acetone. Results analyzed in terms of acetone (C_3) and furfural (C_5) conversion, C_8 and C_{13} selectivities, and carbon balance (C.B.): Mg–Zr (white); Mg–Zr/HSAG300* (light grey); Mg–Zr/HSAG300 (dark grey) and, Mg–Zr/CNF (black).



Figure 4. Initial rates of C₈ and C₁₃ formation. Values obtained with Mg–Zr, Mg–Zr/HSAG300*, Mg–Zr/HSAG300 and Mg–Zr/CNF considering: (a) the total basicity and, (b) the medium-strength basic site concentration.

To compare the final results at the same conditions, product concentrations were normalized considering the total concentration of basic sites; results are shown in Figure 4. Analyzing the C_8 and C_{13} adduct-formation rates and considering the total basic site concentration (Figure 4a), it was observed that all supported catalysts showed a lower C_8 formation rate than the bulk oxide (less noticeable in the case of Mg–Zr/HSAG300).

Concerning the C_{13} formation rate, different behaviors were found: Mg–Zr/HSAG300* and Mg–Zr/CNF showed a very low formation rate, whereas Mg–Zr/HSAG300 showed the highest rate.

Differences between the catalysts were more marked when the reaction rate was defined per medium-strength basic site, which are considered the active sites for aldol condensation (Figure 4 b). Mg-Zr/HSAG300 showed the highest rate for C₈ and C₁₃ production, which was more significant for C₁₃ as it was six-times higher than that of the unsupported catalyst. The results obtained with Mg-Zr/HSAG300* and Mg-Zr/CNF denoted a slight increase in the C8 formation rate but lower values for the C₁₃ adduct formation. The same trends were observed for the reactant conversions: Mg-Zr/HSAG300 showed the highest conversion with similar conversion of furfural (close to 80% in both cases, supported and unsupported) and with increased acetone reduction compared to the bulk material (63.2%). Mg-Zr/HSAG300* and Mg-Zr/CNF showed the poorest performance with less than 45% acetone and 60% furfural conversion in both cases. In addition, carbon balance closures (59.8% with the graphite and 58.3% with the nanofiber) were also low for these two catalysts, suggesting the presence of side reactions. The carbon balance obtained with Mg-Zr/ HSAG300 reached almost 90%, very similar to the bulk oxide.

Acetone self-condensation was previously reported as the main side reaction involving the acetone and the mesityl oxide formation competing with the aldol cross-condensation of furfural and acetone. In the bulk material, the global C₆ selectivity (diacetone alcohol and mesityl oxide) was 4.3% after 24 h reaction time.^[14] For the supported catalyst, the formation of C₆ compounds decreased to values lower than 2% (0.4% with Mg-Zr/HSAG300*, 1.7% with Mg-Zr/HSAG300, and 1.2% with Mg-Zr/CNF). This result is interesting as both reactions are catalyzed by using the same type of active site. It suggests the presence of a synergic effect between the active phase and the carbonaceous support, enhancing those reactions in which furfural and condensation adducts participate. The ratio between mesityl oxide and diacetone alcohol was higher for the supported materials compared to the bulk material. This can be related to the high concentration of weakly acidic sites present on the carbon materials that are needed for catalyzing alcohol dehydration.

To analyze the activity results, three main parameters were considered: the active phase loading, the distribution and concentration of the basic sites, and the role of the support on the adsorption of reactants and products. Concerning the metal loading, analytical results demonstrate poor impregnation over the nanofibers and the graphites prepared by incipient wetness impregnation (Mg–Zr/HSAG300*). The low concentration of Mg–Zr on the catalytic surface caused the reaction development to be difficult; therefore very low amounts of C_8 and C_{13} adducts could be formed. Concerning the basicity, similar distributions of basic sites were obtained for all of the supported materials, except in the case of HSAG300* in which no bidentate sites were observed (corresponding to the catalytically active sites for aldol condensation). Consequently, the absence of these sites hindered the aldol condensation.

It has been demonstrated in previous works that mediumstrength basic sites (corresponding to bidentate adsorption modes of CO₂ on the surface) are catalytically active for aldol condensation.^[14] For the first condensation reaction (formation of C₈ adduct), similar behavior was observed for both the bulk mixed oxide and for the CNF-supported catalyst, whereas the catalysts prepared by incipient wetness impregnation did not show this type of basic site. However, the HSAG-supported catalyst prepared by coprecipitation was four times more active for this reaction than the other catalysts. This trend was sharply augmented for C₁₃ adduct formation, with the reaction rate per unit of active site seven times higher than for those corresponding to the bulk oxide.

A synergic effect of the carbonaceous materials can be inferred from this and the behavior observed for acetone selfcondensation. Carbon surfaces adsorb organic compounds, increasing the strength of this interaction as molecular weight, presence of heteroatoms, and the number of multiple bonds increases.^[29] Therefore, this interaction is expected to be weaker for acetone than for furfural and even more for the condensation adducts. If the active phase is well dispersed (as in the case of Mg-Zr/HSAG300), it will lead to local increases in the reactant surface concentrations in the vicinity of the active phase, thus increasing the reaction rate. In contrast, if the active phase is poorly dispersed, this effect will be negligible (as in the case of the other supports). This effect also justifies the lower conversions obtained for acetone self-condensation observed with the supported catalyst, despite this reaction being catalyzed by the same active sites.

Considering the effect of metal loading, good distribution and concentration of the basicity, and high dispersion of the mixed oxides, the best results were obtained with Mg–Zr/ HSAG300. To study the role of the morphological properties of the graphites on their performance, HSAG materials with similar chemical properties but different morphologies were tested. Mg–Zr was supported on HSAG100 and HSAG500 and results obtained were compared with those obtained with HSAG300, summarized in Figure 5.



Figure 5. Activity results obtained in the aldol condensation catalyzed by different graphites (after 24 h reaction time): Mg–Zr/HSAG100 (white), Mg–Zr/HSAG300 (light grey); Mg–Zr/HSAG500 (dark grey). Results analyzed in terms of acetone (C₃) and furfural (C₅) conversion, C₈ and C₁₃ selectivities, and carbon balance (C.B.).

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Concerning the reactant conversion, similar results were obtained in all cases, with less than 10% difference between them. Although metal-oxide dispersion increases as the surface area increases (Table 2), the final conversion does not show any systematic trend, suggesting again that the support affects catalyst performance. The product selectivity results were also very similar in the three cases, as well as the carbon balance closure. The differences between them were less than 5% if both products are considered together, which is consistent with the similar medium-strength basicity. Considering each product independently, higher C_{13} selectivity was obtained with Mg–Zr/HSAG500 (55%), whereas Mg–Zr/HSAG300 provided higher C_8 selectivities.

The results were analyzed in terms of the initial reaction rate expressed by the total concentration of both basic sites (Figure 6a) and the concentration of medium-strength basic sites



Figure 6. C_8 and C_{13} formation rates. Values obtained with Mg–Zr/HSAG100, Mg–Zr/HSAG300 and Mg–Zr/HSAG500 considering: (a) the total basicity, and (b) the medium-strength basic site concentration.

(Figure 6 b). The differences between the catalysts are much lower than those found for the first set of experiments. The reactivity trends of HSAG100 and HSAG500 can be explained in terms of the concentration of the medium-strength basic sites, HSAG300 showed slightly lower activities than expected, especially in the case of C₈ formation. The higher acidity of Mg–Zr/ HSAG300 (compared with the other HSAG) can explain the low C₈ formation rate, considering that aldol condensation is a reversible process and that the acidic sites catalyze the reverse reaction. The similarity of the reaction patterns suggests the absence of mass-transfer effects (as pore diameters vary from 8 to 17 nm) and that the only role of the dispersion of the active phase is the formation of new active basic sites.

Catalytic stability

The stability of the supported catalysts was studied by performing a second reaction cycle with the used catalyst. Catalysts used in the first reaction cycle were filtered and dried at 373 K before being used in a second reaction cycle. This second reaction cycle was performed under the same conditions and a constant reactant/catalyst ratio.

The obtained selectivities after 24 h on stream are summarized in Figure 7. Mg–Zr/HSAG100 and Mg–Zr/HSAG500 present



Figure 7. C₈ and C₁₃ selectivities obtained after two reaction cycles (24 h each cycle) with Mg–Zr/HSAG100, Mg–Zr/HSAG300 and Mg–Zr/HSAG500. Results after the first cycle (light colors), and second cycle (dark colors).

higher stability and less than 30% difference between the first and second cycle for C_{13} selectivity. The same experiment is reported in a previous study for bulk Mg–Zr, showing that C_{13} selectivity decreases by more than 85%.^[14]

Mg-Zr/HSAG300 showed the poorest results, with 65 and 76% loss of selectivity towards C_8 and C_{13} , respectively. These differences are consistent with the temperature-programmed oxidation (TPO) analysis of the spent catalysts, shown in Figure 8, which depicts the CO₂ released during the temperature-programmed treatment of the spent catalysts in an oxidizing atmosphere. TPO of the fresh materials are also shown by the dashed lines, coke deposits are identified as the difference between the signals corresponding to used and fresh samples. The coke blocks most of the active centers, as confirmed by Brunauer-Emmett-Teller (BET) analysis: N₂ physisorption onto the Mg-Zr/HSAG300 spent catalysts indicated less than 20% of the original surface area: 45.1 m²g⁻¹. The blockage of pores in the other catalysts was less noticeable, with spent catalyst areas of 72 m²g⁻¹, in the case of Mg–Zr/HSAG100 (66% of the original area), and 270 m^2g^{-1} in the case of Mg–Zr/HSAG500 (80% of the original value).

The observed deactivation pattern is explained considering both the surface chemistry and the morphology of the sup-



Figure 8. TPO of the catalyst after 25 h reaction time: (a) Mg–Zr/HSAG100; (b) Mg–Zr/HSAG300; (c) Mg–Zr/HSAG500. Broken lines are profiles corresponding to the same fresh catalyst.

ports. The deactivation of the bulk mixed oxide is attributed to the formation of insoluble condensation products, also catalyzed by basic sites, covering the active sites of the catalyst (leaching effects were not observed under the operating conditions for bulk or for supported catalysts).^[14] Similar deactivation patterns were expected for the supported catalysts, as reactions leading to the formation of these insoluble products are catalyzed by the same sites as the desired reaction. However, the deactivation is markedly lower for the supported catalysts, suggesting that the support plays an important role in altering the reactions involved. When the size of the mixed oxide particles (Table 2) and the average pore diameter (Table 1) were compared, it was observed that the HSAG100 support was most likely to result in active-phase crystallites within the pore. This support showed the highest reusability ratio and this is attributable to its larger pore diameter, which increases further upon impregnation. This suggests that shape selectivity effects hinder the formation of carbonaceous deposits. Shen et al.^[30] suggested using modified Y-zeolites as catalysts for this reaction (pore diameter about 0.7 nm) to introduce important shape selectivity effects, favoring the formation of C₈ versus C₁₃. In the case of HSAG-supported catalysts, pore diameters are higher and do not affect C₁₃ formation rates, but they do hinder the formation of heavier condensation products.

Molecular diameters of furfural and condensation adducts were estimated by Shen et al.,^[30] providing values from 0.57 (furfural) to 0.74 nm (C₁₃ adduct). However, the same authors remark that these molecules (especially the adducts) are highly non-spherical, with critical sizes (length) of up to 1.4 nm (C₁₃ adduct). Therefore, the ratio between the molecule and pore diameters is close to 0.1 in the least favorable case (C13 adduct and narrowest pore). If it is considered that heavier condensation products present both larger molecular diameters and more non-spherical character, shape selectivity effects can tune the formation of these carbonaceous deposits. The HSAG300supported catalyst presents the worst behavior because of the lowest pore and crystallite ratio, suggesting that an important fraction of the active phase is not in the porous structure, therefore not achieving the shape limitations for coke formation.

Reaction mechanism and kinetic model

The presence of mass-transfer effects has been ruled out by ensuring that both particle size and stirring the reaction mixture do not affect obtained results and also by theoretical considerations.^[31] The study of liquid–solid mass transfer and the Thiele-modulus-based efficiency factor for internal diffusion demonstrated that external mass transfer is largely faster than intrinsic reaction kinetics and the efficiency factor is close to one.^[32, 33]

The reaction mechanism of the aldol condensation catalyzed by heterogeneous catalysts (mixed oxides) was discussed in previous works,^[14] concluding that the rate-determining step is the abstraction of the α -proton on the acetone that was previously adsorbed over the catalytic surface by medium-strength basic sites (bidentate centers). Once the enolate is formed, the reaction can proceed via reaction with another acetone molecule, yielding the C₆ by-product, or with a furfural molecule, yielding the C₈ adduct. This adduct also has an α -proton that can be abstracted to provide a new enolate able to react with another furfural molecule yielding the C₁₃ adduct.

According to this mechanism a single power law kinetic model was developed, in which both C_8 and C_{13} formation rates follow first-order dependence on the acetone and C_8 concentrations (enolizable species) and zero-order dependence on furfural concentration. The kinetic data are summarized in Table 3, and the ability of the model to predict the evolution

Table 3. Kinetic constants (min ⁻¹) for the fitting of the experimental results to the proposed kinetic model. ^[a]								
Catalyst	<i>k</i> ₁	<i>k</i> ₂	<i>k</i> ₋₁	<i>k</i> _2	r ^{2 [b]}			
MgZr MgZr/HSAG100 MgZr/HSAG300 MgZr/HSAG500	0.0021 0.0069 0.0065 0.0070	0.006 0.0018 0.0034 0.0042	0.004 0.0014 0.0019 0.0016	0.076 0.0025 0.0024 0.0028	0.97 0.94 0.96 0.96			
[a] Reaction 1: condensation of acetone and furfural yielding C ₈ units; Reaction 2: condensation of C ₈ and furfural yielding C ₁₃ adduct. [b] Goodness of fit.								



Figure 9. Comparison between experimental and kinetic model fitting concentrations of furfural (\blacksquare), acetone (\bullet), C₈ (\bullet), and C₁₃ (x) for the catalysts: (a) Mg–Zr/HSAG100, (b) Mg–Zr/HSAG300, and (c) Mg–Zr/HSAG500.

of reactants and products is shown in Figure 9. In Table 3, values of Mg–Zr (bulk material) were also shown to compare the data obtained.

The kinetic constant values were very similar in the three cases, which is in accordance with the similarity of the catalysts. Data obtained are consistent with the activity results such that supported catalysts have higher values of k_1 and lower values of k_{-1} compared to the bulk material, which implies greater final selectivity of the C₈ adduct. Mg–Zr/HSAG300 shows the highest value of k_{-1} of the three supported catalysts, consistent with the hypothesis of a higher influence of retro-aldolization. The k_2 values of the supported materials were all lower than those obtained with the unsupported materials; however, in the case of Mg–Zr/HSAG100 and 20% higher than the corresponding Mg–Zr/HSAG300 value. This result is in good agreement with the C₁₃ selectivities obtained.

Conclusions

Mg–Zr mixed oxides supported on mesoporous carbon materials are very promising catalysts for the furfural–acetone aldol condensation. Supporting the active phase, the concentration of basic sites exposed to the reactants increases and an increased activity is achieved.

The lack of anchoring sites for mixed oxides on the carbon nanofibers hinders the deposition of the active phase over this surface, and poor results were obtained for this catalyst. Concerning the graphites, the coprecipitation method leads to the most regular disperson of the active phase on the support.

Mg–Zr/HSAG catalysts achieve higher conversion (96.5% for furfural for the HSAG100 support) and higher C₈ and C₁₃ selectivity (80–90%) than the bulk oxide (considered as the most active catalyst for this reaction). These activity trends are related to the more favorable basic strength distribution as well as to the interactions of the reactant with the carbon surface.

It has been demonstrated that it is possible to minimize the deactivation caused by the deposition of heavy condensation products by tuning the morphology of the carbonaceous support.

Experimental Section

Catalysts preparation

HSAG100, HSAG300 and HSAG500 were kindly supplied by Timcal S.A. (Switzerland). PR-24-HHT carbon nanofibers (<0.2% Fe) were supplied by Applied Sciences (Cedarville, OH). These materials were used as supports to increase the activity of the oxides by increasing the dispersion, trying to keep the oxide loading constant and the same Mg/Zr ratio as in the bulk material (Mg/Zr = 4). Supported materials were prepared by using two different methods: incipient wetness impregnation and coprecipitation. Mg–Zr/HSAG300* was synthesized by incipient wetness impregnation of the mixed oxide precursor so-

lution using the carbon support (5 g). Aqueous solution (2.35 cm³) was prepared with magnesium nitrate hexahydrate (0.455 g) and zirconyl nitrate (0.037 g). The metal oxide loading was limited by the low solubility of the zirconyl precursor. The impregnated support was stirred in NaOH solution (500 mL, pH 10) for 1 h. The material was then filtered, washed until it reached pH 7, and dried at 373 K. Finally, it was treated using a He flow at a heating rate of 3 Kmin⁻¹ until the temperature reached 873 K. Mg–Zr/CNF, Mg–Zr/ HSAG100, Mg-Zr/HSAG300, and Mg-Zr/HSAG500 were prepared using the coprecipitation method according to the procedure described by Winter et al.^[16] Supports (5 g) were suspended by constant stirring in 500 mL of a solution containing 25.45 g of the magnesium salt and 2.02 g of the zirconyl precursor. 25 wt % NaOH solution was added until the pH value was 10 and the final solutions were kept stirring for 1 h. They were filtered, washed, and dried at 383 K in an oven before being treated using a He flow with a heating rate of 3 Kmin⁻¹ until 873 K.

After analyzing their morphological and physical-chemical properties, as well as their behavior as catalysts in the furfural-acetone cross condensation, the coprecipitation method was chosen as the preparation technique.

The bulk material, Mg–Zr oxide, was chosen because of its higher activity demonstrated in our previous study.^[14] It was synthesized using the sol–gel technique described by Aramendía et al.,^[34] prepared by dissolving 50.9 g of magnesium nitrate hexahydrate

(Fluka, >99.0%) and 4.04 g of ziconyl nitrate (Aldrich, hydrated) in 1 L of deionized water. The mixture was stirred at room temperature, and aqueous NaOH (Prolabo, 98%) solution was added until the pH value was equal to 10. The gel was aged for 72 h, filtered, and washed with deionized water until pH 7. It was dried at 393 K over 24 h and finally calcined in O₂ (100 cm³ min⁻¹) at 873 K for 3 h at a heating rate of 5 K min⁻¹.

Catalyst characterization

The specific surface area and pore volume were analyzed by N₂ adsorption at 77 K in a Micromeritics ASAP 2020 by using the BET method (to calculate the surface area) and the Barrett-Joyner-Halenda (BJH) approach (to determine pore volume and diameter). The crystallographic structures of the supported materials were determined by XRD using a Philips PW 1710 diffractometer, working with a CuK_{\!\alpha} line (λ =0.154 nm) in the 2 θ range between 5° and 85°, at a scanning rate of 2° per min. The active-phase loading of the catalysts was determined by ICP-OES using SPECTRO-CIR-OSCCD ICP-spectrometer. Approximately 50 mg of the sample was inserted into a Teflon bomb; HF (4 mL), HCl (1 mL), and HNO₃ (0.5 mL) were added. The sample was dissolved in a microwave oven, diluted with deionized water, and analyzed in the spectrometer. The oxides particle morphology and size distributions were determined by TEM by using a MET JEOL-2000 EX-II microscope, and the surface ratio Mg/Zr was investigated by SEM. The analysis was conducted in a MEB JEOL-6100 with EDX analyzer.

The concentration and strength distribution of the basic/acidic sites were determined by TPD of preadsorbed CO_2 or NH₃ in a Micromeritics TPD/TPR 2900. Samples (10 mg) were treated with He at 723 K for 2.5 h and then exposed to a CO_2 or NH₃ (2.5% NH₃ in He) stream at 323 K until saturation coverage was reached. Weakly adsorbed CO_2 or NH₃ was removed by flushing with He at the same temperature for about 1 h 30 min. The temperature was then increased at a heating rate of 5 Kmin⁻¹ from 293 to 923 K, and CO_2 or NH₃ evolution was monitored by mass spectrometry. After the reaction, carbonaceous deposits were characterized by using TPO, which used the same apparatus as the TPD experiments. A carbon sample (10 mg) was maintained in a stream of O_2 /He (2%:98%) at 323 K for 30 min before being heated to 1200 K at 5 K per min.

The surface composition of the mixed oxides was measured by XPS, using a SPECS system equipped with a Hemispherical Phoibos detector operating in a constant pass energy, using MgK_a radiation (hv = 1253.6 eV). The samples were fixed to the sample holder using a carbon adhesive tape. The background pressure in the analysis chamber was kept below $4 \cdot 10^{-9}$ mbar during data acquisition. As samples are non-conducting, surface neutralization during measurements was required.

Reaction studies

The furfural and acetone aldol cross-condensation was carried out in a stirred batch autoclave reactor (0.5 L, Autoclave Engnieers EZE Seal, 500 mL) equipped with a proportional-integral-derivative (PID) temperature controller and a back-pressure regulator. The reactor was loaded with 0.25 L of an aqueous solution of furfural (Panreac, 98%) and the catalyst (500 mg, with an average particle diameter of 50–80 nm). Air was purged by adding N₂, up to 15 bar, three times before starting the condensation reaction. Acetone (Panreac, 99.5%) was introduced to start the reaction, resulting in 5% of organic compounds in aqueous solution (furfural/acetone molar ratio of 1:1). Then, the reactor was pressurized to 10 bar with N₂, heated to reaction temperature, and stirred at 1000 rpm for 24 h. Samples (12–15 samples of 1 mL) were withdrawn from the sampling port during the condensation reaction. Samples were filtered, extracted with ethyl acetate, and analyzed by performing gas chromatography with a Shimadzu GC-2010 equipped with a flame ionization detector (FID) and using a 15 m long CP-Sil 5 CB capillary column as the stationary phase. Peak assignment was performed by fractionation with HPLC and analysis by GC–MS using standard calibration mixtures, following the same procedure as in our previous work.^[15]

Deactivation studies were carried out by collecting the solution obtained after the first reaction with the catalyst in suspension and filtering with a 2-micron mesh. The catalyst obtained was then used in a new reaction with fresh reagents, keeping the same conditions of temperature, reagent concentration, pressure, stirring, and organic/catalyst ratio. Samples obtained were analyzed following the same protocol as in the first cycle.

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