

Designed synthesis of nanostructured ZrO₂ as active support for glycerol valorization reaction

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ABSTRACT

Designed synthesis of nanostructured ZrO₂ as support for glycerol valorization reaction was investigated. The nanocasting route was used to obtain the ZrO₂ support possessing well-dispersed Cu and Zn nanoparticles. The solids were fully characterized by High-resolution transmission electron microscopy (HRTEM), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Electron paramagnetic resonance (EPR), N₂-physisorption isotherms, Temperature-programmed desorption of ammonia (NH₃-TPD), Scanning electron microscopy coupled to energy dispersive spectroscopy (SEM-EDS) and Fourier transform infrared (FTIR) spectroscopy measurements. The resultant CuZn/ZrO₂ catalyst presented here was distinguished by its unique mesostructured features and defective sites formation. The promotional effect of Cu nanoparticles on the activity illustrated that the formation of active acid sites of medium to strong strength can be modulated by adding a second metal to the catalyst. All these properties provided active solids for acetalization of glycerol with aldehydes and ketones due to the interaction between the active centers and the nanostructured support. Density functional theory (DFT) calculation showed the most favorable mechanistic route of low energy for biofuel additives production.

1. Introduction

Nanostructured ZrO₂ has attracted lots of research interests over the past decades with a rapidly expanding range of applications, including in electronics, catalysts, biomedicine, magnetism and thermal barrier coatings [1–5].

Much literature has been reported confirming that the zirconia-based solids are expected to have interesting properties as catalysts or catalysts supports for a variety of reactions [6–9]. Specifically, the recent literature focusing on the nanostructured zirconias has demonstrated that the acidity, porosity, surface lattice oxygen and high surface area to volume ratio typical of the nanostructures may provide good catalytic performances in many reactions [2,7–9]. Most of these Zr-based catalysts are shown to be effective catalysts for biomass valorization in comparison with titania, transition metal oxides, silica,

aluminosilicates, carbon-based materials, alumina and zeolites [7, 10–13].

In particular, biomass valorizations through catalytic reactions became available, once the marginal value of crude glycerol produced from the biodiesel industry can be upgraded properly to produce biofuel additives [14–17]. Currently, acetalization of glycerol in the presence of carbonyl compounds (AG reaction) such as aldehydes and ketones has gained much attention owing to the fact that crude glycerol is converted to high-value 1,3-dioxolane and 1,3-dioxane products [15–17]. Both cyclic five-membered and six-membered oxygen-containing compounds are known as solketal and acetal, respectively (Fig. 1). Moreover, these value-added cyclic compounds are vastly used as fuel additives, solvents, cosmetics, pharmaceuticals and also in perfumery industries [11, 16,17].

The main hindrance constraining for AG reaction commercial

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application is associated with the requirement of a stable solid with catalytically active sites. Irrespective of the reaction conditions employed, the solids should selectively produce the cyclic acetals without leaching out their active sites [11,17]. Although the acid-catalyzed AG reaction occurs in the presence of Brønsted or Lewis acid catalysts, the solids gradually deactivate with time intervals of use. As with almost all acid-base catalysts, these solids afford low selectivity to the cyclic compounds [12–17]. In the case of redox catalysts, the surface oxidation of the active sites along with their strong adsorption of glycerol oligomers by the active phase are among the main drawbacks to effectively use these kinds of solids in the AG reaction [14–16].

Therefore, the stability of supported zirconias may offer effective impact, in terms of cyclic acetals production by combining the well-defined nanostructured features, porosity and controllable acidity. This represents significant advantages in overcoming the leaching of the active sites and selectivity to cyclic acetals during the AG reaction, comparing with the conventional ZrO_2 [6,16].

We herein report the synthesis of mesostructured supported zirconia-based catalysts following the innovative nanocasting route to obtain efficient catalysts for AG reaction with aldehydes and ketones. The physicochemical features of the solids are also investigated in detail by the characterization techniques. Remarkably, the different mechanism of the AG reaction has been illustrated experimentally in a few reports [13,19]. The possible mechanistic pathways for biofuels additive production by DFT studies are examined for the first time, as it has considerable importance in both academic research and industrial development.

2. Experimental

2.1. Catalyst synthesis

The nanostructured supported ZrO_2 -based catalysts were synthesized by a modified nanocasting route using the SBA-15 as hard template. Details on the preparation of the solids can be found in a previous work [18]. For the synthesis of the solids, about 2 mL furfuraldehyde (2-furaldehyde, Sigma-Aldrich) were slowly dropped into the SBA-15 (0.2 g) under magnetic stirring for 10 min, and then a 4 mL of zirconium acetate solution (Sigma-Aldrich) was added to the mixture. The latter reaction mixture was stirred for a further 0.5 h to obtain the SBA-15@C nanocomposite. After that, the mixture was stirred at room temperature for 24 h, the infiltration of both metal and carbon sources into the SBA-15 pores was performed twice. Subsequently, the solid product was recovered and dried in an oven at 100 °C overnight followed by calcination in the absence of air at 500 °C for 6 h to give a final SBA-15@CZr nanocomposite. The product was treated with 1% hydrofluoric acid solution and washed with a copious amount of deionized water to finally be separated by centrifugation. This procedure aims to remove the hard silica-based template giving the ZrO_2 powders for further characterization.

2.2. Metals impregnation

The impregnation of Cu into ZrO_2 was performed in a rotatory evaporator using 3.7 g of the support along with a 20 mL of copper nitrate solution for 2 h. The powder product was collected by filtration, dried at 80 °C for 2 h and finally calcined at 300 °C at a heating rate of 5 °C. min^{-1} for 6 h. The catalyst is represented as Cu/ ZrO_2 .

A Zn-containing ZrO_2 was prepared in the presence of just ZrO_2 following the same procedure by impregnating a 20 mL of zinc nitrate solution and the final solid was denoted as Zn/ ZrO_2 . Similar procedures were adopted to prepare Cu–Zn/ ZrO_2 by impregnating zinc and copper nitrate solutions simultaneously.

To summarize, nanocasted SBA-15@CZr and ZrO_2 samples were produced. Samples possessing 1 wt% of the first metal were denoted as Zn/ ZrO_2 , and Cu/ ZrO_2 whereas the calculated amounts of the metals for CuZn/ ZrO_2 was 0.5 wt% for each metal impregnated.

2.3. Catalysts characterization

X-ray diffraction (XRD) measurements were carried out on a DMAXB Rigaku using a Cu-K α emission radiation at 40 kV and 40 mA. XRD patterns were recorded in the range $2\theta=20\text{--}60^\circ$ with an angle step of 0.02° and time step of 40 s per step.

Fourier-transform infrared (FTIR) spectra were collected in a spectrometer Vertex 70 V (Bruker) spectrophotometer in the range of 400–4000 cm^{-1} at a resolution of 4 cm^{-1} . Before measurements, the catalysts were mixed to a 1 wt% of KBr and pelletized to acquire the spectra.

Scanning electron microscopy (SEM) images were performed on a FEI, Quanta 200 FEG electron microscope. The energy dispersive spectroscopy (EDS) system coupled to the SEM microscope was used for determination of the elemental distributions of the catalysts at 2 kV.

Nitrogen physisorption analyses were performed in the ASAP 2000 instrument. Samples were evacuated for 12 h at 150 °C in vacuum, prior to the analyses. The Brunauer–Emmett–Teller (BET) method was used to determine the surface areas. Pore size distributions were estimated by Barrett–Joyner–Halenda method (BJH) method. The t -plot method was used to obtain the micropore areas and external volumes of the solids.

X-ray Photoelectron Spectroscopy (XPS) analyses were performed on a Physical Electronics VersaProbe II Scanning XPS photoelectron spectrometer equipped with monochromatic X-ray Al K α radiation source. The binding energies calibration at 284.8 eV was used as reference.

High-resolution transmission electron microscopy (HRTEM) images were collected on a JEOL JEM 2010F microscope operating at 200 kV. Prior to the analysis, samples were dispersed ultrasonically in ethanol, and then deposited on carbon-coated copper grids.

Electron paramagnetic resonance (EPR) were recorded on a Bruker spectrometer. The spectra were gained at the X-band microwave frequencies with a field modulation of 9.5 GHz. Before measuring the spectra, samples were treated with helium at room temperature. The magnetic field values were integrated for X-band spectra and the data

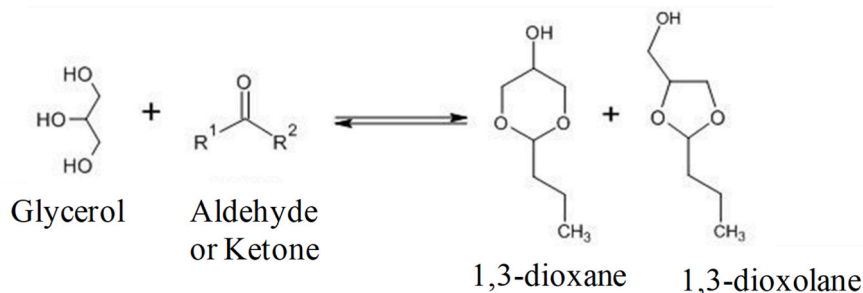


Fig. 1. Scheme of the acetalization of glycerol with aldehydes or ketones to produce cycle compounds. The terms R_1 e R_2 indicates the CH_3 and H, respectively.

were interpreted to obtain the g factor.

Temperature-programmed desorption of ammonia (NH_3 -TPD) experiments were recorded using a Chembet-3000 Quantachrome. Before the measurements, about 100 mg of the solids were placed on U-tube, and then pretreated under the flow of He at 120 °C for 2 h. After samples cooling down to 100 °C, a 5% of NH_3 diluted in He was introduced into the tube. Subsequently, ammonia was replaced by helium at the same conditions for 1 h and desorption was performed from 50 a 350 °C to obtain the TPD profiles.

2.4. Catalytic assessments in AG reaction

Catalytic assessments for AG reaction were carried out in a batch reactor coupled to a thermostatic bath. About 140 mg of the catalysts was placed into the reactor along with the feed consisting of glycerol to substrate molar ratio of 1 at 50 °C. Distinct substrates such as butyraldehyde, benzaldehyde, acetone and furfuraldehyde were also tested in AG reaction.

In such tests, the aliquots of the reaction products were withdrawn in 60 min intervals and analyzed by a gas chromatograph Shimadzu equipped with a FID detector and a capillary column.

The catalytic performance, expressed as the conversion of glycerol and selectivity to the products were determined, as follows:

$$\%X_{\text{Gly}} = \frac{\%mol_{\text{Gly in}} - \%mol_{\text{Gly out}}}{\%mol_{\text{Gly in}}} \quad (\text{I})$$

$$\%sel = \frac{\text{mols of the desired product}}{\sum \text{mol of the converted products}} * 100 \quad (\text{II})$$

where $\%mol_{\text{Gly in}}$ and $\%mol_{\text{Gly out}}$ are mol percentage of glycerol in the feed and mol percentage of glycerol output, respectively.

The reusability of the catalysts was carried out over the most active solids using consecutive batch runs for uses. About 1 wt% of the catalyst mass was added after each run, since some catalyst mass was lost during the experiments. Solutions of glycerol to butyraldehyde molar ratio of 1 were added to the leached solution at 50 °C without any catalyst. This procedure aims to evaluate a possible occurrence of homogenous catalysis achieving no appreciable glycerol conversion within 1 h.

2.5. Density functional theory mechanistic approach

Density functional theory (DFT) studies were carried out to gain insights into the possible mechanistic pathways in AG reaction with butyraldehyde. The computational calculations by DFT were performed by using the Gaussian 09 software package. The molecule optimizations were performed using the Berny algorithm through the M06–2X/6–311+G(d,p) level along with analytic vibrational frequency calculations in order to characterize the obtained structures as minima. The geometry optimizations of reagents and intermediates have been performed similarly to our previously published data [17]. The transition states (TS) structures were obtained from the highest point on the relaxed potential energy surface (PES) at the same theory level. From these data, the mechanistic pathway for AG reaction was shown by the relative energy diagram as a function of the reaction coordinate. All computations were performed in the gas phase.

3. Results and discussion

3.1. Chemical and structural properties

The XRD patterns of the solids are depicted in Fig. 2. The diffractogram recorded for the SBA-15@C nanocomposite exhibits the amorphous nature of the carbonized solid, as expected (Fig. 2 included).

Further filling the Zr and carbon precursors inside the mesopore channels of the SBA-15 template accompanied by calcination steps

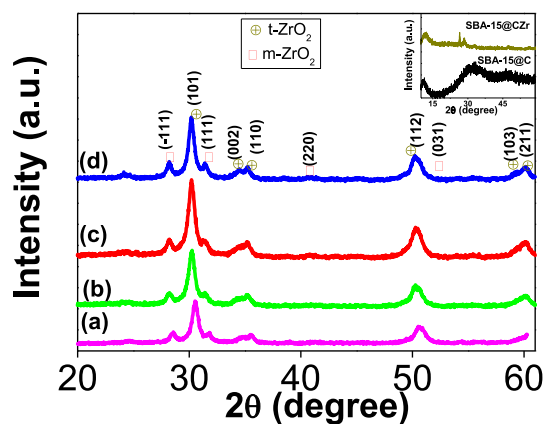


Fig. 2. XRD patterns of the catalyst samples synthesized: (a) ZrO_2 , (b) Zn/ZrO_2 , (c) Cu/ZrO_2 and (d) CuZn/ZrO_2 . The included figures have the XRD patterns of SBA-15@C and SBA-15@CZr nanocomposites.

afforded structural changes in the solids. Accordingly, SBA-15@CZr nanocomposite (Fig. 2 included) depicts low-intensity broad diffraction peaks of ZrO_2 , which are typical of semi-crystalline solids. This suggests that both carbon and Zr precursors fill the pores of the hard SBA-15 template already forming the ZrO_2 phases, after carbonization of the nanocomposite.

Upon removal of the hard SBA-15 template by chemical etching with acid attack, the calcination is necessary to obtain the nanocasted ZrO_2 sample as a reverse replica of the SBA-15 mold possessing small crystallites. Hence, ZrO_2 sample (Fig. 2a) has the tetragonal t- ZrO_2 phase with ill-resolved reflections at 2θ values of 30.2, 34.7, 35.5, 50.3, 59.4 and 60.2°, which are indexed to be from the (101), (002), (110), (112), (103) and (211) lattice planes, respectively (JCPDS 50–1089). Besides, the reflections of monoclinic m- ZrO_2 arise at 2θ values of 28.2, 31.4 and 40.2 and 53.0° matching well with the (–111), (111), (220) and (031) planes (JCPDS 37–1484).

After the occurrence of the t- ZrO_2 crystallite growth process, some of these crystallites are converted into the m- ZrO_2 phase possibly promoted by the calcination at 500 °C. This indicates the prevalence of ca. 81% of tetragonal t- ZrO_2 compared to 19% of the monoclinic m- ZrO_2 phase. The ZrO_2 crystallizes in tetragonal structure with two atoms per unit cell ($Z = 2$) belonging to the $P4/nmc$ (D_{2h}^{15}) space group whereas the m- ZrO_2 is related to the $P2_1/c$ (C_{2h}^5) space group, in accordance with the findings [19,20]. Also, the peak at $2\theta = 24.8^\circ$ could indicate the presence of the (002) reflection for residual graphitized carbon species, as found previously for carbon-based nanocomposites [21,22].

The impregnation of the metals in the nanocasted ZrO_2 accompanied by calcination of the supported solids results in the diffraction intensity increase (Fig. 2b–d). Simultaneously, the tetragonal-to-monoclinic transformation is prevented with both phases coexisting in the solids and most of the crystallites are not big enough to generate strong XRD peaks. Likewise, both m- ZrO_2 and t- ZrO_2 phases are observed for all solids while the tetragonal structure exists as the major phase. Importantly, the absence of standard reflections for CuO and ZnO suggests that these oxides are well-dispersed on the support.

The average crystallite size is estimated by applying Scherrer's equation to the diffraction peaks located $2\theta \approx 30.2^\circ$ (101) from the t- ZrO_2 phase. The sizes range from 13 to 21 nm with the CuZn/ZrO_2 holding the highest average crystallite size values owing to double steps of calcination that result in larger crystallite sizes.

FTIR spectra of the solids (Fig. 3) are recorded to confirm the structural features of the solids. The spectra exhibit a strong absorption band in the 3800–3200 cm^{-1} region, which is attributed to the stretching vibration of hydroxyl groups (ν_{OH}) from adsorbed water molecules [13, 23,24]. At 3500 cm^{-1} , stretching vibration of structural OH groups is also identified. Another band at 1650 cm^{-1} is assigned to the bending of

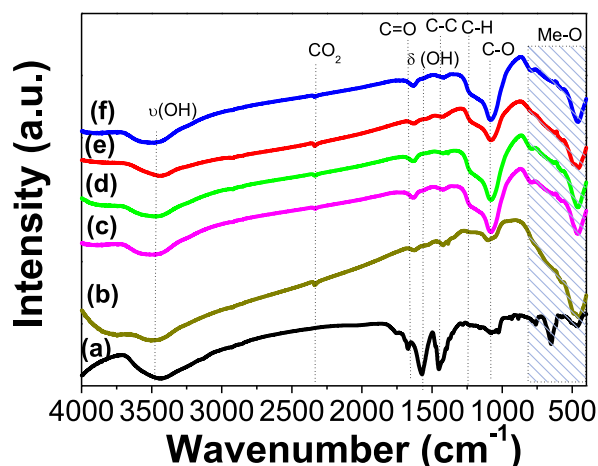


Fig. 3. FTIR spectra of the catalyst samples studied: (a) SBA-15@C, (b) SBA-15@CZr, (c) ZrO₂, (d) Zn/ZrO₂, (e) Cu/ZrO₂ and (f) CuZn/ZrO₂.

OH groups (δ OH) on solid surface, as previously reported [22–25]. The absorption bands of SBA-15@C (Fig. 3a) appearing at 1758 (C=O), 1470 (ν C–C), 1350 (δ C–H) and 1171 (ν C–O) are attributable to the furfuraldehyde precursor [13]. At 2490 cm^{−1}, the CO₂ adsorbed on the samples is clearly visible.

The carbonization of the SBA-15@CZr nanocomposite (Fig. 3b) reveals that most of the carbonaceous bands have their intensity decreased. This is consistent with the formation of a (002) plane from graphitized carbon, as suggested by XRD characterization. Additionally, the processes of silica removal and calcination of the supported solids result in the occurrence of absorption bands below 900 cm^{−1} (Fig. 3c–f). Accordingly, these sharp and intense bands correspond to the stretching vibration of Me–O such as Cu–O, Zn–O and mainly Zr–O bonds [19,23,24]. Of importance, the bands 455 and 577 cm^{−1} are associated with t-ZrO₂ phase, whereas those at 500 and 791 cm^{−1} are ascribed to the m-ZrO₂ ones [21]. This confirms the previous results of XRD that detected the presence of both phases in all solids.

3.2. Valence state and surface composition

EPR spectra are performed to identify the valence state of the supported samples. EPR spectra exhibit two hyperfine signals for the magnetic field values between 0 and 6000 Gauss (Fig. 4). The polymorphs of ZrO₂ in tetragonal and monoclinic structures have similar features with EPR intensities reflected in both intrinsic point defects presence and Zr⁴⁺ ions concentration, as reported elsewhere [26,27]. Moreover, the g factor obtained by the X-band frequency has a value of approximately 2.004 from the symmetric and weaker signal observed in the 3400–3600 Gauss region (Fig. 4 included).

This probably implies in electrons inside the oxygen vacancies forming the F-centers, which corroborates with the findings [26]. Given the synthesis conditions and calcination in air, the g factor at 1.979 and 1.958 for both bulk and surface sites of Zr³⁺ ions are unobservable in the present samples. Remarkably, the surface-localized O^{2−} superoxide radical ion depicts a rhombic EPR signal at about $g_z = 2.033$, $g_y = 2.0096$ and $g_x = 2.0034$, typical of zirconia-based samples [27]. Thus, the EPR spectrum suggests that the superoxide presence in the supported samples can not be ruled out.

Noteworthy, EPR signals of Cu/ZrO₂ and CuZn/ZrO₂ samples do not allow distinguishing the contribution of Cu components since they are overlapped with those of Zr. Accordingly, the assignments of the EPR signals for Cu consist of prominent signals with axial symmetry (included Fig. 4) having $g_{||}(2.38) > g_{\perp}(2.04) > g_e(2.02)$ due to the Cu species with anisotropic coordination environments, as in case of distorted octahedral Cu²⁺ ions in an isolated state [27,28]. Another signal

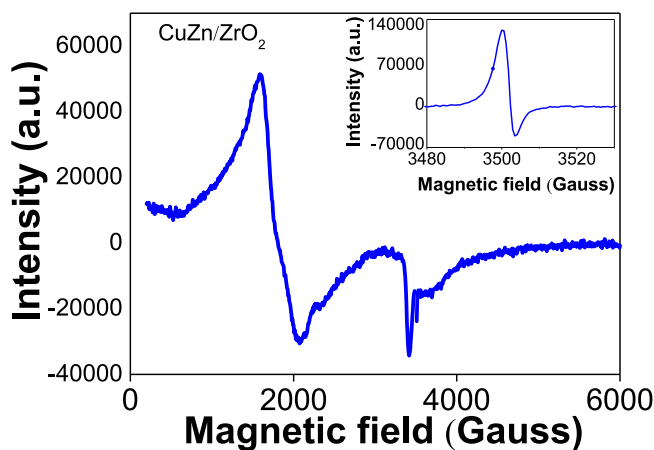
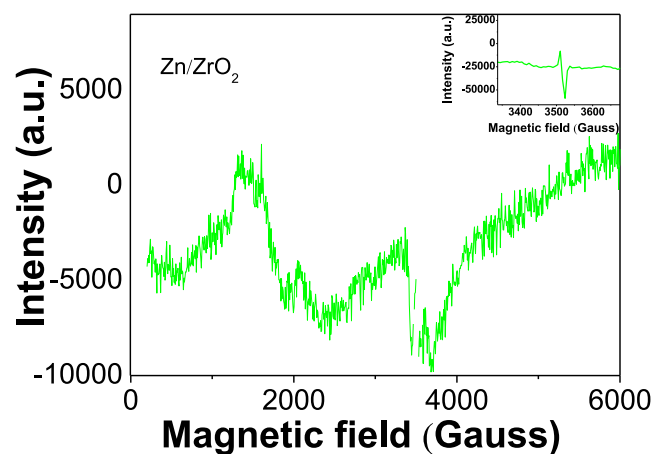
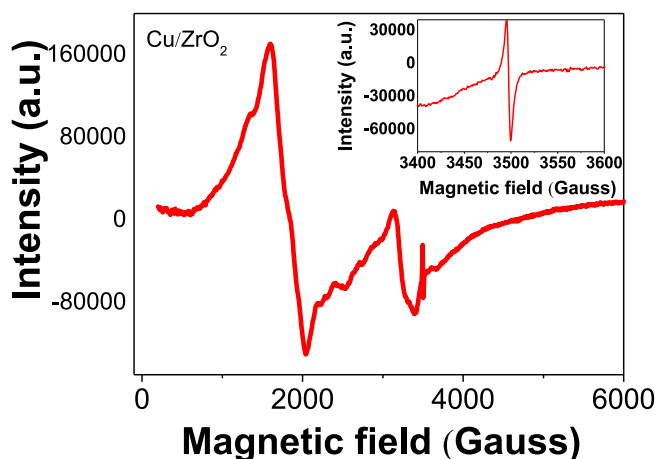


Fig. 4. EPR spectra of the supported catalyst samples studied. The included figures are the EPR spectra in the 3400–3600 Gauss.

at $g = 2.23$ is a single line shape due to the magnetic interaction of two or more adjacent Cu²⁺ ions [24,28]. A closer look at the region of 2000 Gauss also suggests a broad signal attributable to the Cu²⁺ ions in strong dipolar interactions caused by mutual interactions of the paramagnetic Cu²⁺ ions in well dispersed CuO particles on ZrO₂ [28].

The EPR signal of Zn/ZrO₂ sample is characterized by a low-intensity broader signal at about 3500 Gauss (included Fig. 4) along with another

board signal at approximately 2900 G. These signals are assigned to the isolated paramagnetic centers with the existence of isolated oxygen vacancies [29]. In addition, the g factor of about 2.002 is found for Zn/ZrO₂ and CuZn/ZrO₂ samples being consistent with the values for shallow donor centers due to the interstitial Zn and surface O vacancy, as found elsewhere [29,30]. Particularly, the anisotropic signals with $g_{||} = 2.384$ and $g_{\perp} = 2.095$ in CuZn/ZrO₂ sample may suggest the interaction between Cu²⁺ and ZnO with ZrO₂ support, in a similar fashion as Cu doped zinc samples [30]. As ZnO is dispersed on ZrO₂ surface, the oxygen vacancies signals can be overlapped with those of Zr⁴⁺ ions, when compared with the CuZn/ZrO₂ spectrum. EPR results are in accordance with XRD and FTIR measurements that suggest the presence of ZrO₂ in all solids.

To further get insight about the valence states and to ensure the surface chemical compositions of the catalysts, XPS analyses are performed. The binding energies taken from XPS spectra are summarized in Table 1.

All samples exhibit two sets of binding energies at 182.2 and 184.6 eV corresponding to the Zr 3d_{5/2} and 3d_{3/2} lines, respectively (Table 1). These results illustrate that organic and zirconium precursors loaded inside of the pores of the silica matrix give the final replica, in which zirconium exists as Zr⁴⁺, when carbonized [31,32]. In full agreement with the XPS data, XRD results show both t-ZrO₂ and m-ZrO₂ phases in all solids. The binding energies shift for lower values for Zr 3d_{5/2} core level in all samples, in comparison with the literature reports [33]. This suggests a strong Zr attraction by outer electrons. Such a decrease of the binding energy of 0.3 eV further reveals that the oxygen vacancy defects and their concentration have increased in the solids. Accordingly, EPR results indicate the presence of the O²⁻ species and oxygen vacancies defects, as well.

Furthermore, C 1s lines of SBA-15@CZr reveal a diversity of functional groups. Accordingly, the C 1s contribution at 284.8 eV is due to the graphitized sp²-carbon species coming from the carbonization process of the solid [24,34], as observed by XRD. Importantly, the fitted component of carbon species at 284.8 eV may also correspond to the C-C, C=C, and C-H bonds and adventitious carbon, as well. The contribution at 286.2 eV is associated with the hydroxyl (C-OH). At 289.9 eV, the uppermost oxidized carbon species e.g., C=O/COOH is likely [24,34]. The formation of these species is mainly ascribed to the existence of the functionalization of the carbon species during the carbonization process. As stated above, the functionalized carbon species bonded to the ZrO₂ support have very significant amounts of oxidized carbon species. This observation is also associated with the

FTIR results of SBA-15@CZr sample.

Meanwhile, the residual silicon and fluoride ions appear with the contributions of the Si 2p and F 1s core levels at BE of 104.0 and 684.4 eV, respectively.

XPS spectra of the CuZn/ZrO₂ sample for Zr 3d, O 1s, C 1s, Cu 2p and Zn 2p core levels are illustrated in Fig. 5. As stated above, Zr 3d core level (Fig. 5a) is deconvoluted into sets of spin-orbital doublets assigned to the Zr⁴⁺ ions, again consistent with the XRD and EPR results. The O 1s core level spectrum (Fig. 5b) is fitted with three contributions. The asymmetric main peak is located at 530.4 eV that may be attributed to the surface oxygen and lattice oxygen species and whilst at 532.5 eV, the surface-absorbed oxygen species such as O²⁻, OH⁻, O⁻ and CO₃²⁻ are in accord with the reported literature [24,35]. Another possibility is that the BE at 532.5 eV can be likely related to the physically adsorbed OH groups [15,24]. Furthermore, the peak at 533.6 eV has a minor contribution, corresponding to C=O bonds and surface adsorbed oxygen species [15]. Noteworthy, the lattice oxygen has a lower intensity peak than that of adsorbed oxygen species, which could indicate the greater amount of oxygen vacancies in the solid that is consistent with EPR results. Such species appear in all supported solids independently of the metal dispersed on ZrO₂.

Remarkably, these results agreed with those shown by the C 1s core level (Fig. 5c) that evidence three contributions of carbon species most probably bonded to oxygen. Despite that the carbon components are unchanged for the supported samples, their intensities have greatly decreased indicating that they are partially removed by the nanocasting and calcination processes. Silicon also remains for all catalysts suggesting strong interactions among carbon species, silica and ZrO₂ support.

Table 1 illustrates that the surface atomic concentrations of oxygen progressively increased along with the reduction of carbon amounts, which is ascribed to the calcination of the supported solids. For instance, the O/C atomic ratio is 2.2 for SBA-15@CZr while that of Cu/ZrO₂ and CuZn/ZrO₂ is 3.1. It is interesting to note that the Cu/ZrO₂ exhibits very high O/C atomic ratio value of ca. 5.8. This is directly correlated to the creation of oxygen vacancies in the ZrO₂ support as an inverse replica of the SBA-15 and also as a consequence of the various calcination steps submitted to the supported samples.

Besides, the Cu 2p region is fitted with the Cu 2p_{3/2} and Cu 2p_{1/2} core lines being visible at 932.8 and 952.8 eV, respectively (Table 1). Although these binding energies in Cu/ZrO₂ and CuZn/ZrO₂ samples match well with those observed Cu²⁺ (CuO) and Cu¹⁺ (Cu₂O) and CuO_x species [24,36], the values are slightly shifted from those presented in

Table 1

Binding energies (BE) values and O/C, Zn/Zr and Cu/Zr surface atomic ratios of the catalysts obtained by deconvoluted XPS spectra.

Catalyst	Zr 2p	Zn 2p	Si 2p	F 1s	O 1s	Cu 2p	C 1s	O/C	Zn/Zr	Cu/Zr
SBA-15@CZr	182.5	–	104.0	684.4	530.4	–	284.8	2.2	–	–
	184.6				532.5		286.2			
					533.6		289.9			
Cu/ZrO ₂	182.2	–	103.6	–	530.2	932.8	284.6	5.8	–	0.07
	184.6				532.1	934.5	285.9			
					533.3	941.7	289.0			
						943.8				
						952.8				
Zn/ZrO ₂	182.2	1022.4	103.4	684.9	530.3	–	284.6	3.1	0.16	–
	184.6				532.2		285.7			
					533.4		288.8			
CuZn/ZrO ₂	182.2	1022.2	103.5	684.6	530.2	933.0	284.8	3.1	0.11	0.17
	184.6				532.1	934.8	286.1			
					533.3	941.6	288.6			
						943.8				
						952.8				
						963.5				

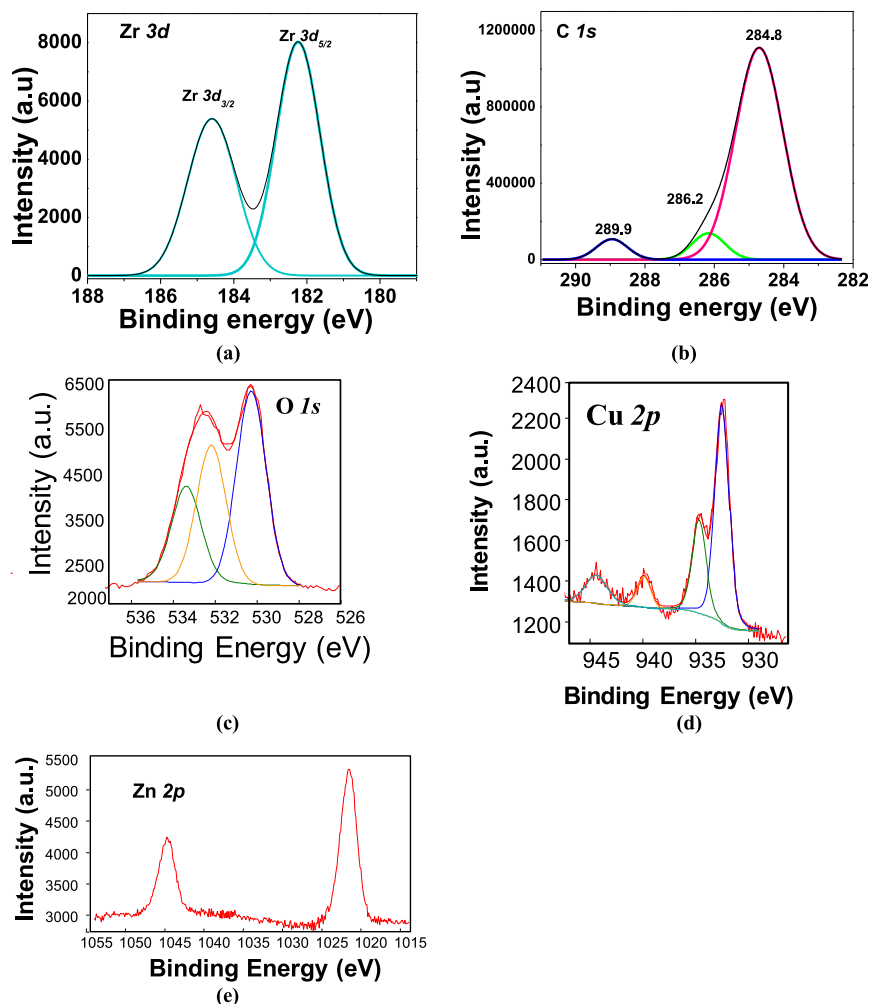


Fig. 5. Representative XPS spectra of the CuZn/ZrO₂ catalyst sample: (a) Zr 2p, (b) C 1s, (c) O 1s, (d) Cu 2p and (e) Zn 2p.

the literature owing to the strong interaction between Cu (Zn) and ZrO₂ support. Literature reports that it is very hard to distinguish between the Cu¹⁺ and Cu⁰ species in the XPS spectra due to the Cu 2p_{3/2} binding energy and peak shape similarities [37]. However, the existence of Cu¹⁺ and Cu⁰ species in the studied solids is obviously unlikely in reason for the oxidation of these species during calcination.

Specifically for Cu 2p_{3/2} core level (Fig. 5d), four spin-orbit doublets are found with the main peak at 932.8 eV, confirming the presence of Cu²⁺ species as CuO [27,36]. Also, the peak positioned at 934.5 eV is ascribed to a covalent Cu²⁺–O bond polarized by Zr⁴⁺ or both Zr⁴⁺ and Zn²⁺ ions, which may result in a drop in the effective charge of Cu²⁺ species [24]. These peaks associated with the two shake-up satellite peaks located at 941.8 eV and 943.8 and a higher energy satellite at 963.5 eV allow recognizing the presence of Cu²⁺ ions [36–38]. This scenario is consistent with the fact that the Cu₂O phase generated during the nanocasting process is converted into CuO upon calcinating the solids, and hence the XPS peaks of CuO are observable.

Moreover, literature reports assign that the X-ray Cu LMM Auger resonance lines are used to identify the Cu–O bonding with BE values of 917.6, 916.5 and 918.5 eV for Cu²⁺, Cu¹⁺ and Cu⁰, respectively [37]. However, we could not identify these lines in the XPS spectra for Cu 2p core levels of Cu/ZrO₂ and CuZn/ZrO₂ samples because they are very noisy. Therefore, the single peak at 917.8 eV reinforces the assumption that Cu mainly exists as Cu²⁺ from CuO as the dominant species.

XPS spectra of Zn-containing samples depict two main peaks for Zn

2p region. The first peak is at 1022.0 and 1045.2 eV (Fig. 5f), which may be characterized by Zn 2p_{3/2} and Zn 2p_{1/2} core levels [29]. Moreover, the Auger line of Zn LMM is almost in the same position of C 1s and Zr 3d core levels, and thus it is impossible to distinguish Zn²⁺ from Zn⁰ at 2p level.

Furthermore, the highest ratio of Cu/Zr in CuZn/ZrO₂ sample (Table 1) suggests a good dispersion of Cu²⁺ species on the support. This is likely due to a change in the chemical environment of the ZrO₂ by lattice deformation, which is induced by both calcination and deformation of Zr as well as Cu and Zn entities being in a strong interaction with ZrO₂ support. Consequently, high amounts of ZnO and CuO phases on the support surface are observed. Hence, these results indicate the surface enrichment of copper-based entities, whereas Zn/Zr atomic ratio (Table 1) decay evidences the low surface coverage of Zn²⁺ species in the CuZn/ZrO₂ sample.

3.3. Textural and morphological properties and acidity

The textural properties of the solids through N₂-physorption isotherms reveal that the SBA-15 mold has a type IV isotherm with H₁ hysteresis, as shown in our earlier studies [18,39]. This curve is typical of ordered mesoporous materials possessing narrow pore size distribution and cylindrical pores [18]. These observations are consistent with textural properties results in Table 2.

The carbonaceous SBA-15@CZr nanocomposite has a type IV

Table 2

Textural properties of the studied solids obtained from N₂-physisorption analyses.

Sample	BET surface area(m ² .g ⁻¹)	Pore volume (cm ³ .g ⁻¹)	t-plot Micropore area(m ² .g ⁻¹)	Pore size (nm)
SBA-15	794	0.84	105	2.4
SBA15@CZr	46	0.05	7	1.0
ZrO ₂	206	0.22	4	3.2
Cu/ZrO ₂	83	0.10	7	2.3
Zn/ZrO ₂	99	0.14	2	2.4
CuZn/ZrO ₂	100	0.14	10	2.4

isotherm with hysteresis loop between H₁ and H₂ (Fig. 6a). Significant modification of the isotherm with changes in the hysteresis shape is seen after incorporating Zr followed by carbonization to produce the nanocomposites. Accordingly, the observed closure of the hysteresis loop points of SBA-15@CZr towards P/P₀ values of 0.40, in comparison with that of pristine SBA-15. This implies the cavitation-induced evacuation of the adsorptive through the constricted interconnected mesopores [18, 40, 41]. Another possibility is that the SBA-15@CZr nanocomposite has slightly smaller pores similar to other carbonized materials [39–41]. This is further evidenced by pore size distribution curves.

Upon removing the silica matrix followed by calcination, the nanocomposite is converted into an ordered mesoporous structure of ZrO₂, which is indeed an inverse replica of SBA-15, where nitrogen accessibly enters in its pores. Thus, a type IV isotherm with H₁ hysteresis loop is registered for ZrO₂ sample (Fig. 6a) with the capillary condensation at the relative pressures between 0.7 and 0.8. After impregnating the metals on ZrO₂, the N₂-physisorption isotherms show the preservation of the ordered mesoporous structure without changes in the isotherm shape and hysteresis loops (Fig. 6a).

As expected, SBA-15 hard template has the highest textural properties values with a narrow pore size distribution centered at 2.4 nm whilst

the SBA-15@CZr holds the lowest ones owing to the carbonization process (Table 2). Among the supported oxides, the CuZn/ZrO₂ and Zn/ZrO₂ exhibit the same surface area of ca. 100 m² g⁻¹ and pore volume of ca. 0.14 cm³ g⁻¹ while the BET surface area and pore volume of Cu/ZrO₂ decay to 83 m² g⁻¹ and 0.10 cm³ g⁻¹. Although the supported metal oxides have well-dispersed nanoparticles on ZrO₂ surface, the drop in the BET surface area and comparable decrease in pore volume are possibly due to the metal nanoparticles deposition on both surface and into the ZrO₂ support mesopores. As a consequence, the pore filling is observed (Table 2).

Remarkably, the pore size distributions of the nanocasted solids are relatively broad, owing to the defective mesopores structures, and micropores creation upon calcination of the solids, as well. Also, Table 2 illustrates that the pore filling and carbonization of the SBA-15 mold to obtain SBA-15@CZr affect pore size distributions. This causes a shift towards smaller pore sizes of ca. 1.0 nm for SBA-15@CZr compared to those of pristine SBA-15. In the case of the nanocasted solids, ZrO₂ sample evidences the formation of uniform mesopores with average sizes of 3.2 nm, after silica removal and subsequent calcination processes. The pore sizes noticeably shift towards lower pore widths regions along with a gradual decrease in the intensity due to the pores partially plugged by the nanoparticles, as further demonstrated by TEM images.

The t-plot analysis reveals that almost all solids have surface areas contributed by the primary mesopores possessing micropore surface areas ranging from 2.5 to 10 m² g⁻¹ in some extent due to the gases formed during the calcination.

To further investigate the morphology and elemental composition of the solids, SEM-EDS analyses are carried out. The pristine SBA-15@C sample exhibits typical sphere-like platelet morphology of the SBA-15 mold (Fig. 7A₁, first row), which is indeed composed of 63% Si, 23% O and 14% C (Fig. 7A₂, first row). Besides, EDS elemental mapping of SBA-15 reveals a uniform distribution of the elements (Fig. 7A₃, first row). In the case of template mesoporous SBA-15@CZr nanocomposite,

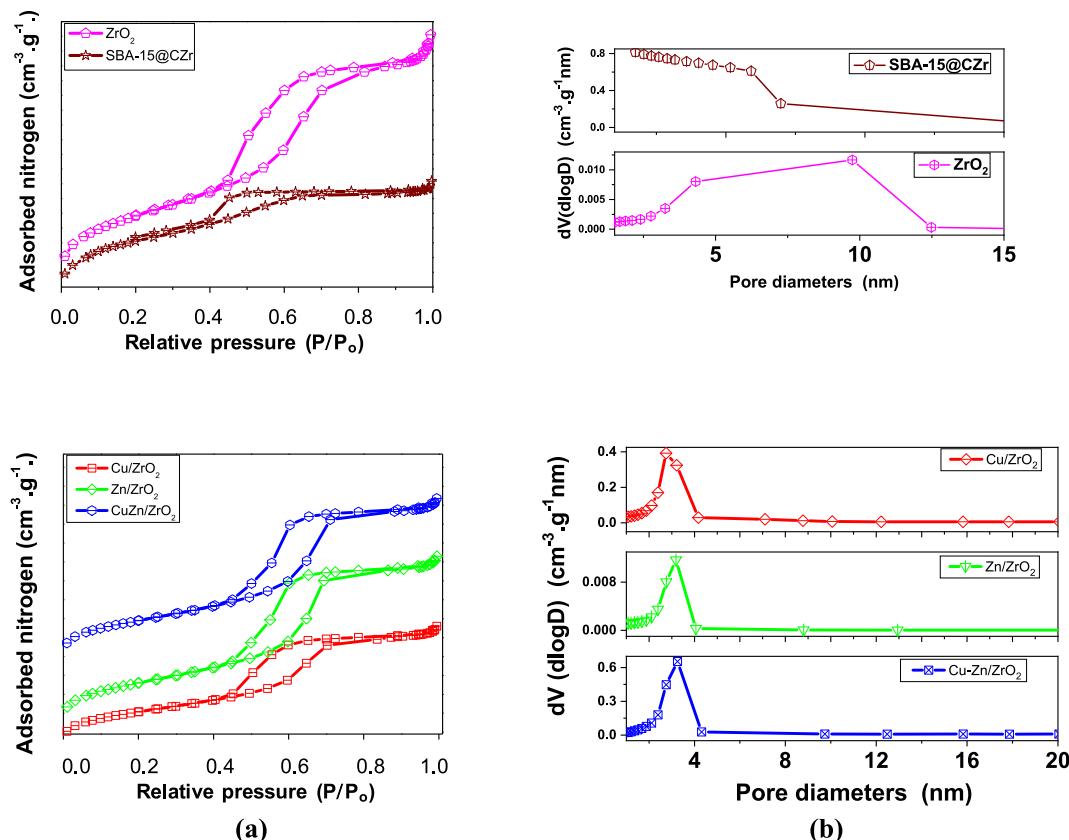


Fig. 6. (a) N₂-physisorption isotherms and (b) BJH pore size distributions of the catalyst samples.

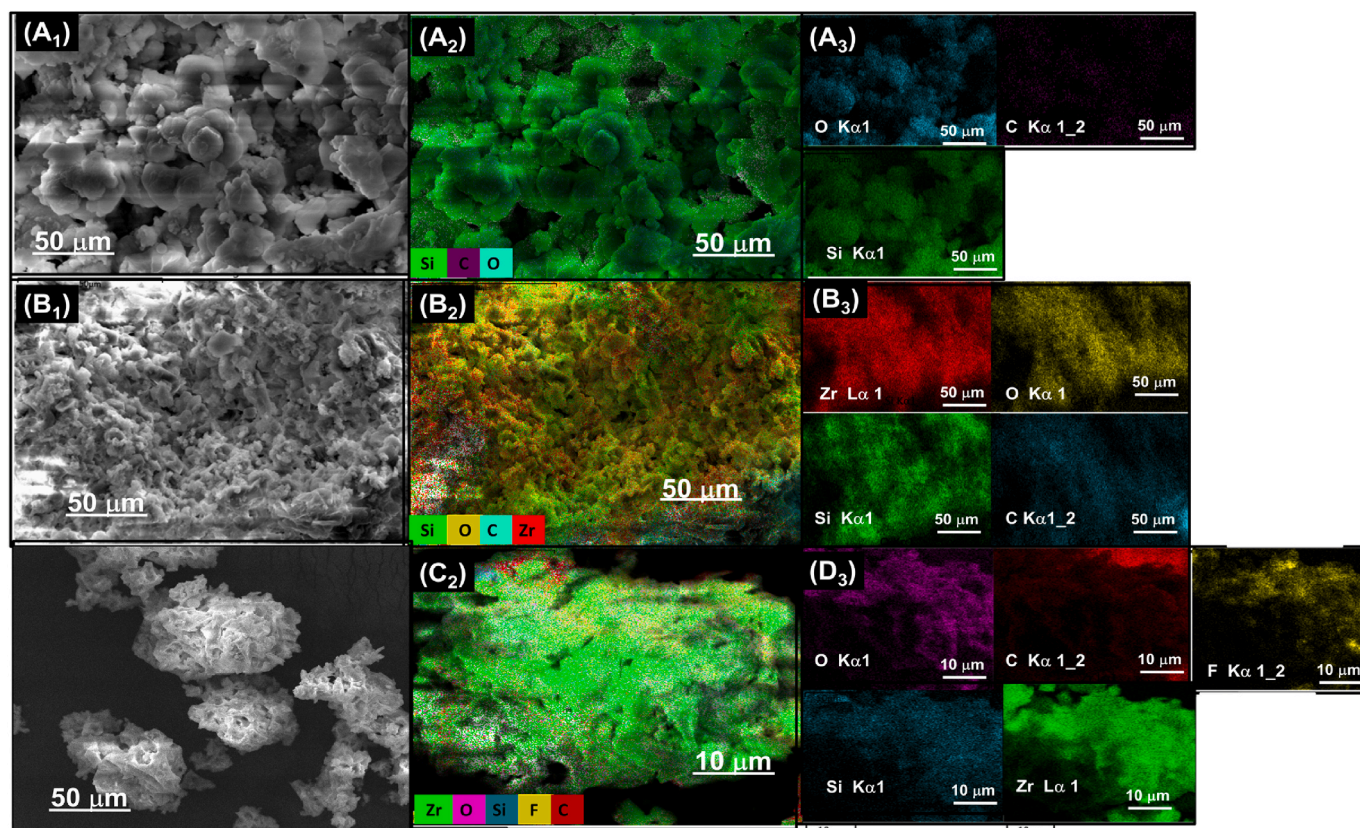


Fig. 7. SEM-EDS micrographs of (A) SBA-15@C, (B) SBA-15@CZr, (C) ZrO₂, (D) Zn/ZrO₂, (E) Cu/ZrO₂ and (F) CuZn/ZrO₂ catalyst samples. The HRTEM micrographs are assigned as (G₁) ZrO₂, (G₂) Zn/ZrO₂, (G₃) Cu/ZrO₂ and (G₄) CuZn/ZrO₂ for the supported catalyst samples.

sphere-like platelets remain present (Fig. 7B₁, second row), which compromises in the morphological integrity of the solid, after both precursor infiltration and carbonization steps. The C and Zr elements confirm the SBA-15 pore filling with the precursors along with Si and O elements (Fig. 7B₂, second row). However, C and Zr random accumulation on the surface evidences the lack of uniformity in the dispersion of these elements (Fig. 7B₃, second row).

For ZrO₂ nanostructured replica, the surface morphology clearly reflects the calcination giving aggregated particles (Fig. 7C₁, third row). EDS analyses illustrate the presence of residual Si with content lower than 1% atomic ratio arising from SBA-15. The presence of F coming from the etching with hydrofluoric acid is also observed. Also, C appears in the final material from the furfuraldehyde precursor source, besides the expected Zr element (Fig. 7C₂, third row). Such elements are not well-distributed on solid surface (Fig. 7C₃, third row). This result is consistent with previous textural parameters decrease observed for ZrO₂ sample comparing with those of SBA-15.

Additionally, the ZrO₂ supported solids show similar uneven aggregation of the particles with big voids observable among the platelets in all nanostructured solids, as illustrated by SEM images (Fig. 7D₁, Fig. 7E₁ and Fig. 7F₁ in the fourth, fifth and sixth rows, respectively). Of importance, elemental mappings of all samples show that Zn and Cu elements are not uniformly dispersed on the surface of ZrO₂ plate (Fig. 7D₂ and Fig. 7E₂ in the fourth, fifth and sixth rows, respectively). In other words, Zn and Cu can be on the pores, in agreement with the decrease of the textural properties of the supported solids compared to those of ZrO₂. Also, Cu and Zn with contents lower than 1.0 wt% are clearly seen on the plate ZnO₂ surface, as detected in EDS mapping (Fig. 7D₃, Fig. 7E₄ and Fig. 7F₅ in the fourth, fifth and sixth rows, respectively). Interestingly, EDS images demonstrate that elemental Si is detected in very low amounts in all spectra, which came from the

synthesis residue, as stated before. Particularly, the dissolution of the ZnO nanoparticles during the etching away of the SiO₂ with subsequent calcination is believed to cause the decrease in the Zn content on the solid surface.

Moreover, HRTEM micrographs of selected solids show that the ZrO₂ support (Fig. 7G₁) has a well-ordered framework that can be viewed as a crystalline-nanocasted inverse replica of the SBA-15. The uniform particles with sizes ranging from 2 to 12 nm are observable, in good agreement with those obtained from the XRD data. The TEM micrographs with high magnifications depict regions consisting of ZrO₂ with an interlayer spacing of 0.297 and 0.263 nm, which can be respectively originated from (110) and (220) crystal planes of t-ZrO₂ and m-ZrO₂, respectively. This assumption also agrees with the XRD data that illustrate ZrO₂ phases and reports of the literature [29,31,33]. Some bridges between the crystals are also observed, as illustrated by the arrows (Fig. 7G₁). Similar outcomes are observed for the nanocasted strategy applied for CeO₂ replicated from silica [42]. Meanwhile, few zones where unordered particles are detected can be originated from the silica template, as suggested by SEM-EDS and XPS results.

In addition, the nanocasted Cu/ZrO₂, Zn/ZrO₂ and CuZn/ZrO₂ (Fig. 7G₁-7G₄) exhibit the presence of higher crystallite size domains than ZrO₂ support, despite that the periodicity does not extend over a large region. Although the consecutive steps of calcination submitted to the solids cause high crystallite size domains, the ordered mesoporous metal oxides replicate the siliceous template to a great extent.

Interestingly, the nanoparticles are dispersed on the supports with uniform sizes varying from 1 to 10 nm, as an example of which is indicated by the black dots inside the circles in the micrographs. For Zn/ZrO₂ (Fig. 7G₂), the lattice fringes are measured to be 0.297 and 0.263 nm identifying the crystal planes of t-ZrO₂ and m-ZrO₂. In most parts of the Zn/ZrO₂ larger and unordered particles in an agglomerated zone

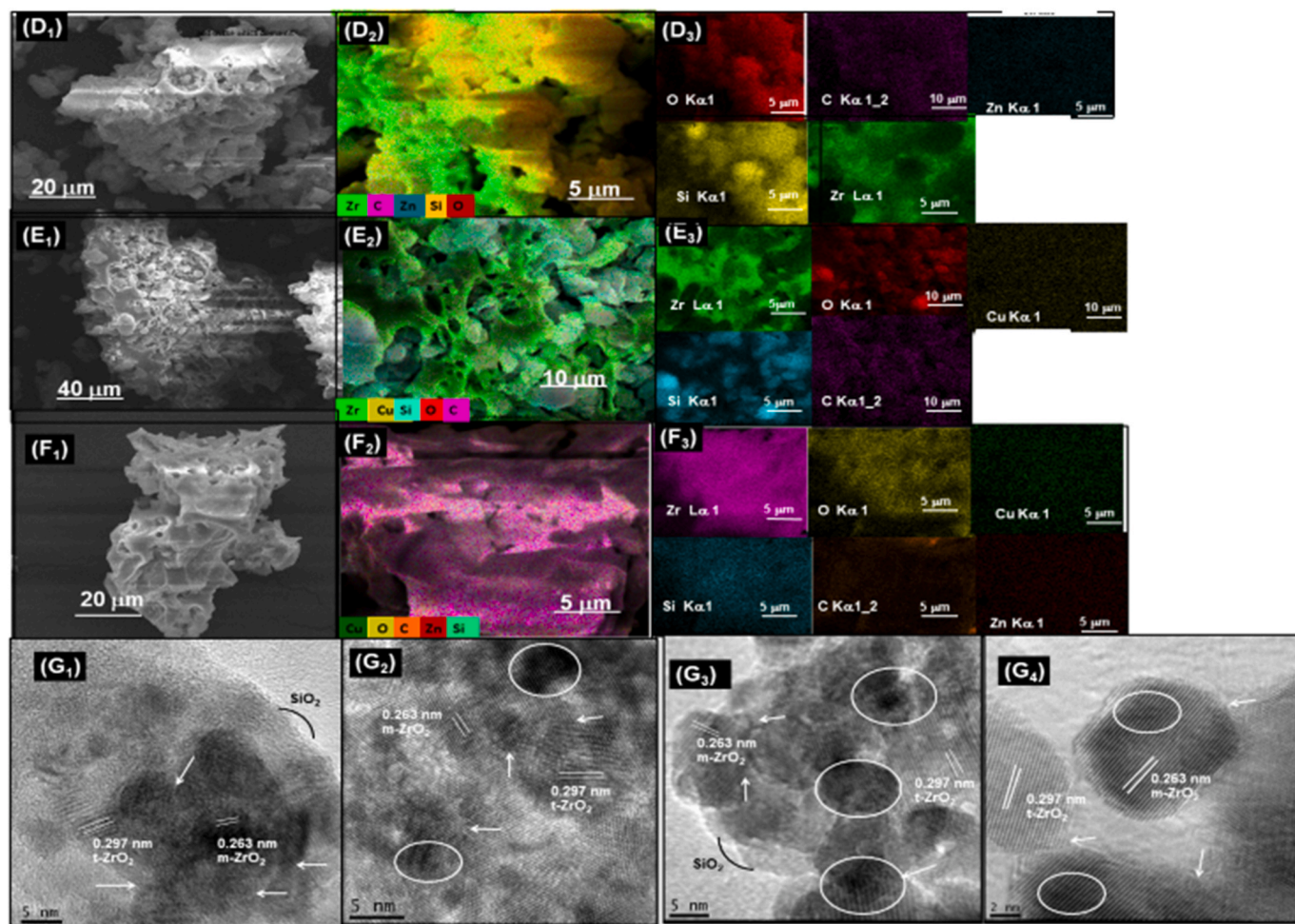
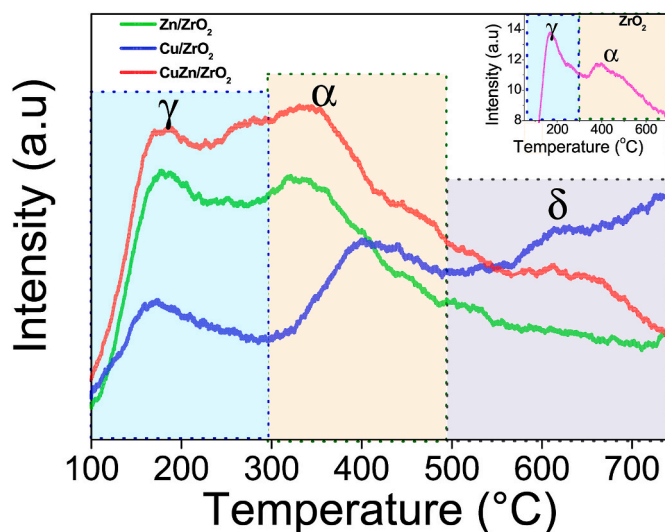


Fig. 7. (continued).

with sizes smaller than 2 nm are seen (inside the circles), which is believed to be in reason of the calcination process. Similar features are detectable in the micrograph of Cu/ZrO₂ (Fig. 7G₃). In the case of CuZn/ZrO₂ (Fig. 7G₄), two well-defined lattice fringes originated from ZrO₂ phases are detected with the CuO and ZnO nanoparticles (inside the circles) having an average size lesser than 5 nm. Therefore, HRTEM micrographs confirm the tailored highly ordered mesoporous ZrO₂ inverse replica formation and the well-dispersed nanoparticles interacting with silica and ZrO₂ support.

Acidity measurements through NH₃-TPD profiles are shown in Fig. 8. The Cu, Zn and Zr metals are considered to be surface hard acid sites and thus, they are expected to bind to the oxygen atom and interact with the adsorbed ammonia molecules. Hence, the cations can bind with a weak base as ammonia in three localized regions (Fig. 8). The first one is named as γ region comprising the 100–300 °C range, which can be associated with the acid sites of weak strength. The broader desorption peak at small temperatures in NH₃-TPD profile region is positioned at 300–500 °C range e.g., α region coming from acid sites of medium strength. The acid sites of strong strengths e.g., δ region are located at temperatures superior to 500 °C, as found elsewhere [43].

Two types of acid sites observed by the γ and α regions of ammonia desorption are detected in all samples, which leads to the assumption that acid sites present in the solids are of weak and medium strengths. Specifically, ZrO₂ holds ammonia peaks appearing with low intensities and widths (Fig. 8 inset) indicating the solid has weak and medium-strength acid sites of very low distribution of strengths (Table S1, supplementary material). This agrees with other studies that demonstrate acid sites of weak to medium strengths are present in ZrO₂ [44,45].

Fig. 8. NH₃-TPD profiles of the supported catalyst samples. The included Figure is the NH₃-TPD curve of ZrO₂ catalyst sample.

In the case of Cu/ZrO₂ and CuZn/ZrO₂ catalysts, peaks are shifted for higher desorption temperatures suggesting that Cu impregnation increase the acidity of the ZrO₂ supported solids that possess both medium and strong strength acid sites, in major amounts. These types of acid

sites in both Cu/ZrO₂ and CuZn/ZrO₂ catalysts are due to the ammonia strongly bound to either Cu or Zn as a consequence of these Lewis acid sites formed on the inter-surface with strong interactions ZrO₂ support. The opposite observation is registered for Zn/ZrO₂, in which the solid contains small amount of medium acid sites as Zn is known to decrease the acidity of ZrO₂-based catalysts [45]. The total amount of acid sites follows the order Cu/ZrO₂ > CuZn/ZrO₂ > Zn/ZrO₂ and ZrO₂. This illustrates that most of the solids have weak and medium strength acid sites. Contrarily, CuZn/ZrO₂ has acid sites of strong strength in greater amounts.

3.4. Catalytic activity in AG reaction

3.4.1. Effect of the reaction time

The catalytic performances of the solids are tested for the acetalization of glycerol with benzaldehyde at 50 °C and glycerol to benzaldehyde molar ratio of 1 (Fig. 9a). Blank runs carried out in the absence of a catalyst demonstrate that negligible glycerol conversion is achieved under the aforesaid conditions. Glycerol conversion experiences a steady increase as the reaction time rises from 60 to 360 min for the nanocasted solids (Fig. 9a). It is reasonable to conclude that prolonging the reaction time much more reacting molecules disrupt their bonds forming new compounds from the new bonds built. For example, ZrO₂ depicts null glycerol conversion immediately after mixing the reactants, and then reaches 8% of conversion within 60 min to achieve 14% of glycerol converted in 360 min of reaction.

Importantly, SBA-15@CZr nanocomposite is an exception because no appreciable glycerol conversion to its cyclic acetals occurs within 360 min owing to its low acidity. On the contrary, glycerol conversions slightly increase beyond 240 min over the nanocasted oxides achieving

maximum conversions in 360 min. Besides, the catalytic performances greatly improved upon dispersing metal oxide nanoparticles on ZrO₂ and glycerol conversion remained almost constant at the end of the reaction.

Among the nanocasted supported oxides, a remarkable catalytic performance for CuZn/ZrO₂ is achieved with 32% of glycerol conversion while the conversion of 24% is found over Cu/ZrO₂ within 360 min. On the other hand, ZnO nanoparticles dispersed on ZrO₂ exhibits almost similarities compared to ZrO₂ catalyst in terms of glycerol conversion of ca. 16 and 14%, respectively. Moreover, glycerol conversion using ZnO and CuO nanoparticles as catalysts is found to be less than the unity in 360 min of reaction.

Irrespective of the catalyst evaluated, glycerol acetals i.e., 1,3-dioxolane and 1,3-dioxane are produced simultaneously with other

Table 3

Conversion of glycerol and selectivity to the products at 50 °C during AG reaction with benzaldehyde. Reaction conditions: glycerol to benzaldehyde molar ratio of 1, catalyst mass 140 mg and reaction time of 360 min.

Sample	Glycerol conversion (%)	%Selectivity		
		1,3-dioxalane	1,3-dioxane	Others ^a
CuZn/ZrO ₂	32	28	8	64
Cu/ZrO ₂	24	32	7	63
Zn/ZrO ₂	16	38	5	57

^a Others include 4,6-tripropyl-1,3,5-trioxane; 2-hydroxypropan-2-yloxy propane-1,2-diol, 1,2,3-propanetriol monoacetate, 2,2-dimethyl- [1,3]-dioxane-4-il-methanol,3-(2-hydroxypropan-2-yloxy)propane-1,2-diol and byproducts of condensation.

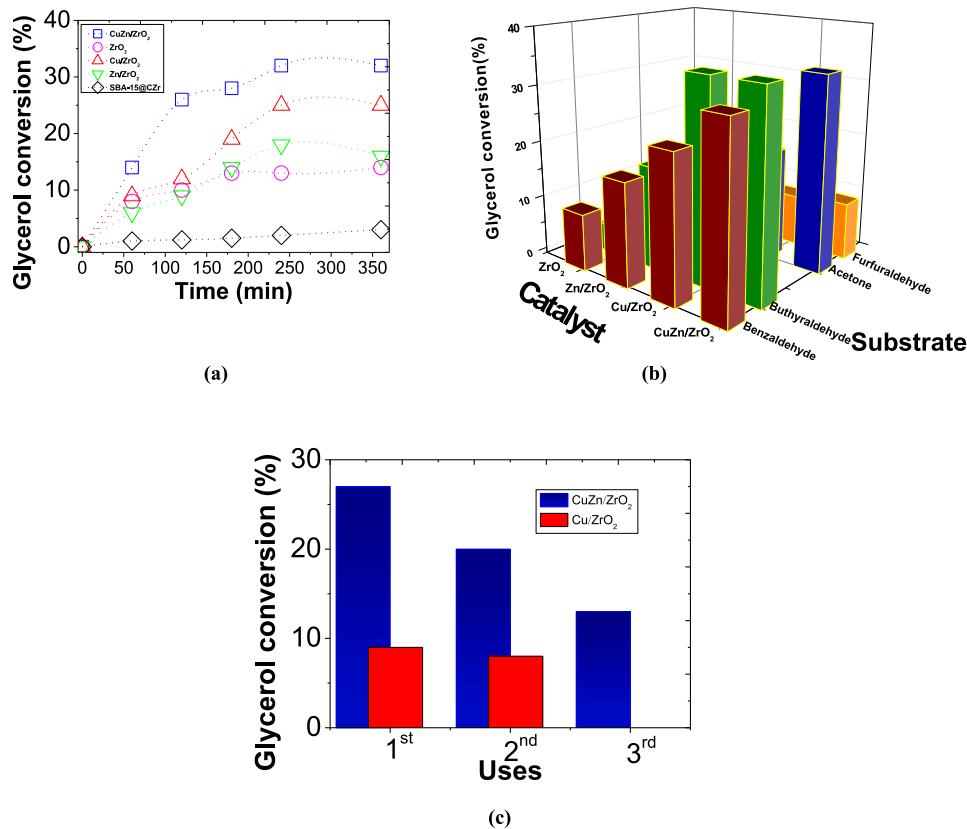


Fig. 9. (a) Catalytic evaluation in function of the reaction time for AG reaction in the presence of benzaldehyde at 50 °C, catalyst mass of 140 mg and glycerol to benzaldehyde molar ratio of 1. (b) Use of distinct substrates for AG reaction at 50 °C, catalyst mass of 140 mg and glycerol to substrate molar ratio of 1. (c) Recyclability studies for the most active solids at 50 °C, catalyst mass of 140 mg and glycerol to butyraldehyde molar ratio of 1.

byproducts being the prevailing cycle compounds (Table 3). Notably, these acetals are formed in the first minutes of the reaction with the achievement of 28% for 1,3-dioxolane selectivity within 360 min.

Hence, catalytic performances seem to be time and acidity dependent. The glycerol is mainly converted within 360 min and the AG reaction is promoted by metal nanoparticles dispersed on ZrO_2 , which may act as acid active sites in favor of the enhancement of the cyclic acetals production. However, the glycerol acetal selectivity severely decays, since the formation of the six-membered-ring acetal is uncommon at longer reaction times, in agreement with the findings [13,46–49]. Moreover, selectivity toward other products remains almost the same for all catalysts.

3.4.2. Acetalization of glycerol over distinct substrates

Catalytic performances in the AG reaction in the presence of various substrates are evaluated at 50 °C (Fig. 9b). As expected, SBA-15@CZr does not show significant glycerol conversion in any substrate used, most probably due to its very low porosity and mild acidity. On the contrary, all other catalysts are active in the presence of the substrates. This keeps consistent with the order of acidity and porosity of the solids. Also, it still shows that glycerol could react with both aldehyde and ketone in distinct ways under the conditions studied.

When the catalysts are exposed to acetone, glycerol conversions illustrate that the reactivity of the acetone towards glycerol is somewhat favorable than aldehydes in reason of the withdrawal CH_3 groups bonded to carbonyl radicals that make acetone more reactive than the aldehydes counterpart.

Among all the aldehydes, the presence of bulky aryl radicals bonded to the carbonyl group as in benzaldehyde make a much greater steric hindrance to the glycerol attack than the aliphatic acetone. Also, furfuraldehyde shows a poor performance within 360 min of reaction is observed owing to the cyclic conformation of the furan-containing oxygen atom causing a repulsion effect to the glycerol molecules. Hence, benzaldehyde is less active than acetone achieving a maximum conversion of 32%. Particularly, the steric hindrance caused by the kinetic diameter of benzaldehyde may slow down the reaction rates making this substrate less active towards glycerol than the butyraldehyde. Moreover, butyraldehyde behaves better than cyclic aldehydes counterparts, in terms of glycerol conversion because of its high polarity. However, selectivities to acyclic acetals are too low, which is attributable to the self-condensation of the aliphatic aldehydes, independently of the catalyst studied.

Notably, high catalytic performances of the solid are closely related to acidity and textural parameters, invariably for all the catalysts. For instance, the porosity of CuZn/ZrO_2 along with its higher number of medium and strong acid sites provided by the better glycerol conversions and 1,3-dioxolane selectivities compared to all other catalysts in study and literature ZrO_2 -based catalysts reports [6,16,19].

Generally speaking, nanoparticles dispersion on ZrO_2 may affect the nanostructured solids performance during AG reaction as follows: (i) in the absence of metals nanoparticles, nanostructured ZrO_2 has elevated textural performance and acidity, despite its modest catalytic performance in AG reaction; (ii) the promotion effect by the nanoparticles dispersed on nanostructured ZrO_2 results in the increased acidity of the solids; (iii) existence of Cu^{2+} catalytically active species along with structural Brønsted acid sites from ZrO_2 itself provide the Lewis acid-base pairs to promote activity and selectivity to the cyclic acetals; (iv) Zn^{2+} species counterpart does not improve significantly the activity under mild conditions; (v) simultaneous presence of well dispersed Cu and Zn nanoparticles gives strong interaction among Cu^{2+} and Zn^{2+} species and the ZrO_2 surface. This results in the acid and basic pairs to activate the reactants and promote better catalytic performances.

In agreement with acidity measurements, the catalytic performances decrease in the order $\text{CuZn/ZrO}_2 > \text{Cu/ZrO}_2 > \text{Zn/ZrO}_2$ that is to say, Zn and Cu species on ZrO_2 modulate the catalytic activity in any condition tested.

3.4.3. Recyclability studies

Once the reaction conditions are optimized, one should expect the stability of the most active solids towards various reaction cycles (Fig. 9c). The butyraldehyde is chosen as substrate to evaluate the stability of the most active catalysts for consecutive cycles of 24 h. As it can be seen, glycerol conversion greatly decreases after recycling Cu/ZrO_2 , since the active sites of the solid are lost, after 1st use and that of CuZn/ZrO_2 is not greatly affected. At the same time, Zn/ZrO_2 catalyst has more similar behavior to that of Cu/ZrO_2 with very low conversion levels in the 1st cycle of use. Thus, the stability of both Cu and Zn species relative to either Cu or Zn alone on ZrO_2 is in line with the fact that the strong interaction of both oxides with the ZrO_2 structure plays an important role in the catalytic performance. After using the solids for 3 consecutive cycles, the monometallic catalysts deactivate entirely, having a considerable amount of metal leached i.e., 50–80%, which indicates a weak interaction of the Cu and Zn nanoparticles alone with the support. Besides, deactivation of the CuZn/ZrO_2 became apparent only after the third use as the glycerol conversion decays to 25% with 13% of 1,3-dioxolane selectivity and a moderate leaching of 25% is observed.

Regarding other physicochemical features of CuZn/ZrO_2 such as its high acidity, the crystal lattice defective sites and porosity seem to contribute for the best performance of the solid. Importantly, all catalysts have similar acid site densities although the acid strength for CuZn/ZrO_2 is greater than the other solids. This makes CuZn/ZrO_2 catalyst more active and stable than Cu/ZrO_2 counterpart. Another feature of CuZn/ZrO_2 is the preferred formation of acetals instead of byproducts after recycling in the liquid phase reaction.

3.4.4. DFT studies for AG reaction in the presence of butyraldehyde

According to mechanistic considerations, it is assumed that the glycerol acetalization as a condensation reaction follows two reversible steps [15,17,48]. In the first step, surface hydroxyl groups of the ZrO_2 support interacts with the double-bond carbonyl group of butyraldehyde to obtain a positive charge intermediate (Scheme in Fig. 10a). This constitutes the slow step of the reaction. Then, a nucleophilic attack by the terminal glycerol hydroxyl groups to the aforesaid intermediate gives a dehydration reaction to form a tertiary carbonium ion. The latter species is resonance stabilized with the non-bonded electron pairs of the adjacent oxygen atom forming a hemiacetal intermediate [17,50]. The consecutive nucleophilic attack of the aforesaid intermediate to the terminal OH groups of glycerol subsequently results in the cyclization step to form a five-membered cyclic 1,3-dioxolane (solketal), being accompanied by the water release (Fig. 10a). These mechanistic considerations are in agreement with the findings [17,51,52]. If another nucleophilic attack of the terminal OH group of the glycerol takes place, the formation of a six-membered cyclic 1,3-dioxane (acetal) is likely (Fig. 10a), as observed earlier [14,50].

Either the formation of acetal or ketal depends on the protonation of the hemiketal, which determines whether these products are formed. However, some findings state that the formation of the five-membered ring is less thermodynamically stable due to the short lifetime of the carbanion ions compared to that of hemiketal, even if the five-membered 1,3-dioxolane is formed favorably [15,17,43].

As there is no consensus about the more favorable route, we perform the DFT studies to have a detailed investigation of the possible mechanistic pathway for 1,3-dioxolane and 1,3-dioxane formation through AG reaction in the presence of butyraldehyde.

Mapping of the electron density surface for glycerol, butyraldehyde, 1,3-dioxolane and 1,3-dioxane molecules are shown in Fig. 10b. The electron delocalization contours of the DFT-optimized structures indicate that the highest accumulation of electrons is in the oxygen atoms of the glycerol molecule. This is in opposition to the low electronic density located in the carbonyl group of butyraldehyde. Thus, the optimized configuration of HOMO depicts high electron density for nucleophilic glycerol, which transfers its electron to the LUMO of the electrophilic butyraldehyde (Fig. S1, supplementary material). Such chemical

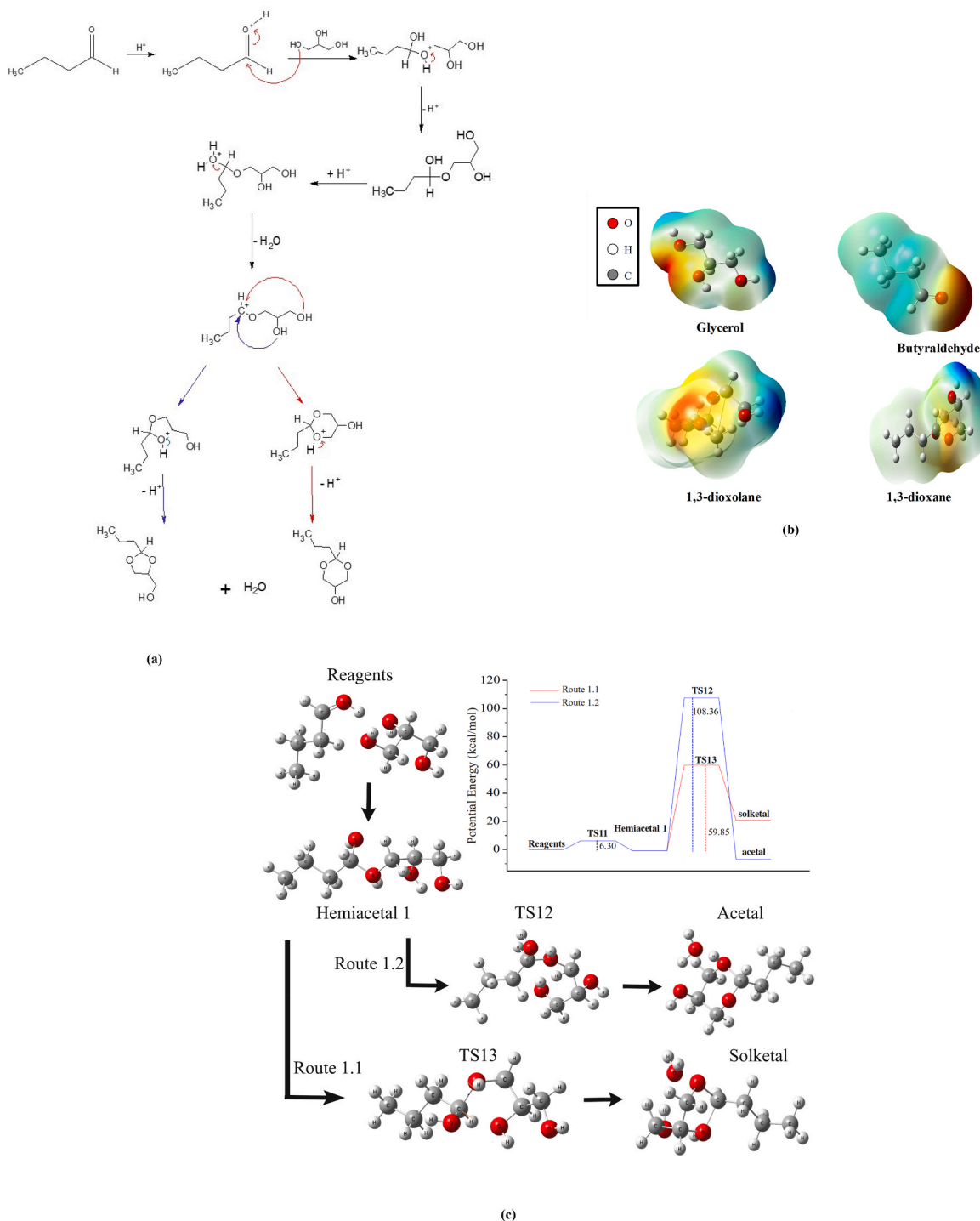


Fig. 10. (a) Reaction scheme of the glycerol acetalization with butyraldehyde representing the steps for 1,3-dioxolane and 1,3-dioxane formation. (b) Mapping of the electron density surface for glycerol, butyraldehyde, 1,3-dioxolane and 1,3-dioxane molecules. (c) The reactant intermediates and products representation as well as relative energies of the reactants transition states and products for AG reaction.

interaction between glycerol and butyraldehyde reactants allows the electron transfer in the frontier orbital.

Additionally, the HOMO and LUMO orbitals will thus be more likely to interact providing the formation of the hemiacetal intermediate, which confirms the formation of the aforesaid glycerol acetals, as proposed in Fig. 10a. These results agree with the model adopted in our previous studies [17]. Accordingly, both 1,3-dioxolane and 1,3-dioxane formation possibly occur as the electron density appears localized on these products (Fig. 10b).

Of the species involved in the reaction, the formation of the products involves HOMO and LUMO interactions (Fig. S1, supplementary material), which are favored by transition states of low energy, when considering a single route of butyraldehyde protonation followed by a nucleophilic attack of a glycerol molecule to yield 1,3-dioxolane [15, 17].

The transition state (TS) energies are calculated to have a deeper understanding of the most favorable route for AG reaction. The results are depicted in the calculated energy diagram in function of the reaction

coordinates (Fig. 10c). The geometric parameters are investigated considering the hydroxyl group of glycerol with the protonated electrophilic butyraldehyde molecule involved in the hemiacetal intermediate formation. As this intermediate would rearrange to form 1,3-dioxolane and 1,3-dioxane, the most favorable route should be analyzed.

The interaction between glycerol and butyraldehyde allows the HOMO and LUMO overlapping to the reaction pathway for hemiacetal and 1,3-dioxolane. The energy of intermediates and transition states (TS) for this route demonstrates that the 1,3-dioxolane formation involves the terminal hydroxyl group of the hemiacetal with the carbonyl of butyraldehyde accompanied by the water release pathways. When the hemiacetal and the carbonyl intermediates rearrange, it is expected to the cyclization reaction occurrence to form 1,3-dioxolane, which constitutes the key step for best-hypothesized mechanism of the reaction.

Calculations afford the possibility of confirming that the aforesaid route for 1,3-dioxolane is the rate-determining one since the HOMO-LUMO interactions are more favorable than that of 1,3-dioxane. As found elsewhere, the experimental investigations demonstrate that the 1,3-dioxolane is the most energetically favorable compound [14,15,52, 53].

Moreover, the cyclization of the intermediate to form 1,3-dioxolane e.g., solketal step is slow leading to the greater HOMO-LUMO gap. At this stage, the transition state (TS11) energies decrease and thereby gaining a significant stabilization in comparison to that of 1,3-dioxane e.g., acetal formation (Fig. 10c).

These observations reasoning provide a basis to justify that the presence of a catalyst is needed to have an energetically favored pathway with low energy of the transition states and thus enhance the reaction rates by the surface acidity of the Lewis sites to form 1,3-dioxolane, as found by other authors [14,50–53].

However, a direct comparison between the possible 1,3-dioxane product route should be discussed since very different molecule configurations are involved. Based on our initial hypothesis, the hemiacetal formation is largely encouraged due to the lowest energy of transition state, as aforesaid.

The optimized structures suggest an increased electron density in the area near the 6-membered ring of 1,3-dioxane, and thereby the former product is predominant for the first route with respect to that of 1,3-dioxolane from the energy of formation considered here. In line with these results, TS diagram for the non-catalyzed reaction shows that the reactant transformation to obtain the hemiacetal 1 requires 6.3 kcal mol⁻¹, which appears as the lowest energy step (Fig. 10c). This agrees with the charge density and HOMO and LUMO interactions described above.

When the energy of the intermediate hemiacetal 1 molecule is considered, two possible pathways can be followed to form 1,3-dioxolane and 1,3-dioxane. In the case of route 1.2, the transition state (TS12) energy increases as the bond weakened lowering the vibration frequency of hemiacetal intermediate 1, which leads to the potential energy of ca. 108.36 kcal mol⁻¹. The latter pathway has much greater energy than that observed for the route 1.1 (TS13), in which the transition state (TS12) has an energy value of ca. 59.85 kcal mol⁻¹. This is in agreement with the experimental reaction routes also observed in the literature that shows the 1,3-dioxane (acetal) formation upon higher energies conditions e.g., higher temperatures is even greater than that for the 1,3-dioxolane (solketal) formation [54]. In this case, 1,3-dioxane is the predominant product with maximum energy requirements inherently due to its lower structural ring tensions avoiding its regioselectivity against 1,3-dioxolane that can be easily formed. Despite the transition state with lower energy promises the easier reaction of 1,3-dioxolane, it has low stability being the kinetic controlled product due to the fact that the transition state formation step is a limiting factor in determining the reaction selectivity.

Based on these findings, the route 1.2 suggests that the spatial arrangements of the intermediates can greatly affect the configuration of the products, increasing the energy of the transition states. Even if the

hemiacetal intermediate formation takes place without steric hindering, the 1,3-dioxolane and 1,3-dioxane formation require favorable energy conditions.

To conclude, the reaction between glycerol and butyraldehyde readily occurs to form 1,3-dioxolane and 1,3-dioxane products with high conversion levels. These products can be converted into byproducts through side reactions depending on the reaction conditions, as experimentally demonstrated.

4. Conclusions

Copper species, such as isolated Cu²⁺ nanoparticles and CuO_x clusters existed dispersed on mesostructured CuZn/ZrO₂ catalysts, which had unique textural, structural and morphological properties compared to its Zn supported-ZrO₂ analog. Even if Zn nanoparticles were well dispersed on nanostructured ZrO₂, the low acidity and poor resistance against leaching during the reaction did not contribute to the activity in the AG reaction. A correlation between the acid strength and the activity was found. Simultaneous addition of Cu and Zn species balanced the acidity of the nanostructured solid providing more Cu active centers for AG reaction in the presence of various substrates. This was due to the defects on ZrO₂ support and the increased number surface Lewis acid sites strongly interacting with the support, which results in more active solids in the reaction. Mechanistic insights by DFT demonstrated the low energy pathway was provided for 1,3-dioxolane and 1,3-dioxane formation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ceramint.2022.09.140>.

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