Supplementary Materials

The morphological aspects and elemental analysis of the solids are investigated by SEM-EDS analyses (Figure S1 in supplementary materials). The unsupported solids exhibit dense plates without specific particle morphologies, as illustrated by the SEM images in Figure S1A. The roughened surfaces of the unsupported solids are consistent with the presence of big particles because they aggregate upon the high calcination temperature employed. In agreement, the evaporation rate, condensation and polymerization processes are among the factors that occurred during the synthesis that arouse the densification and crystallization of the gel to form glassy structures during the calcination of alumina-based compounds [40]. For LA support, ill-defined stacked leaves particles are visible (Figure S1A$_1$) along with the interconnectivity of the particles, as shown by the magnified top view (Figure S1A$_1$, inset). More specifically, the outer surfaces of MA and ZA exhibit a densification in the morphology (Figure S$_1$A$_2$ and Figure S1A$_3$), whereas the lower surface has a porous feature structure (not shown). These types of pores exhibit shrinkage indeed during the transformation of theamorphous gel to the crystallized nanoporous structure, as found elsewhere [40].

Moreover, the EDS image of LA depicts a crumpled surface with the presence of Al, O, La and C elements having atomic percentages of ca. 45.4, 41.5, 9.5 and 3.5%, respectively (Figure S1B$_1$). The La and Al elements are indeed well dispersed on the surface, according to the EDS mapping (Figure S1C$_1$).

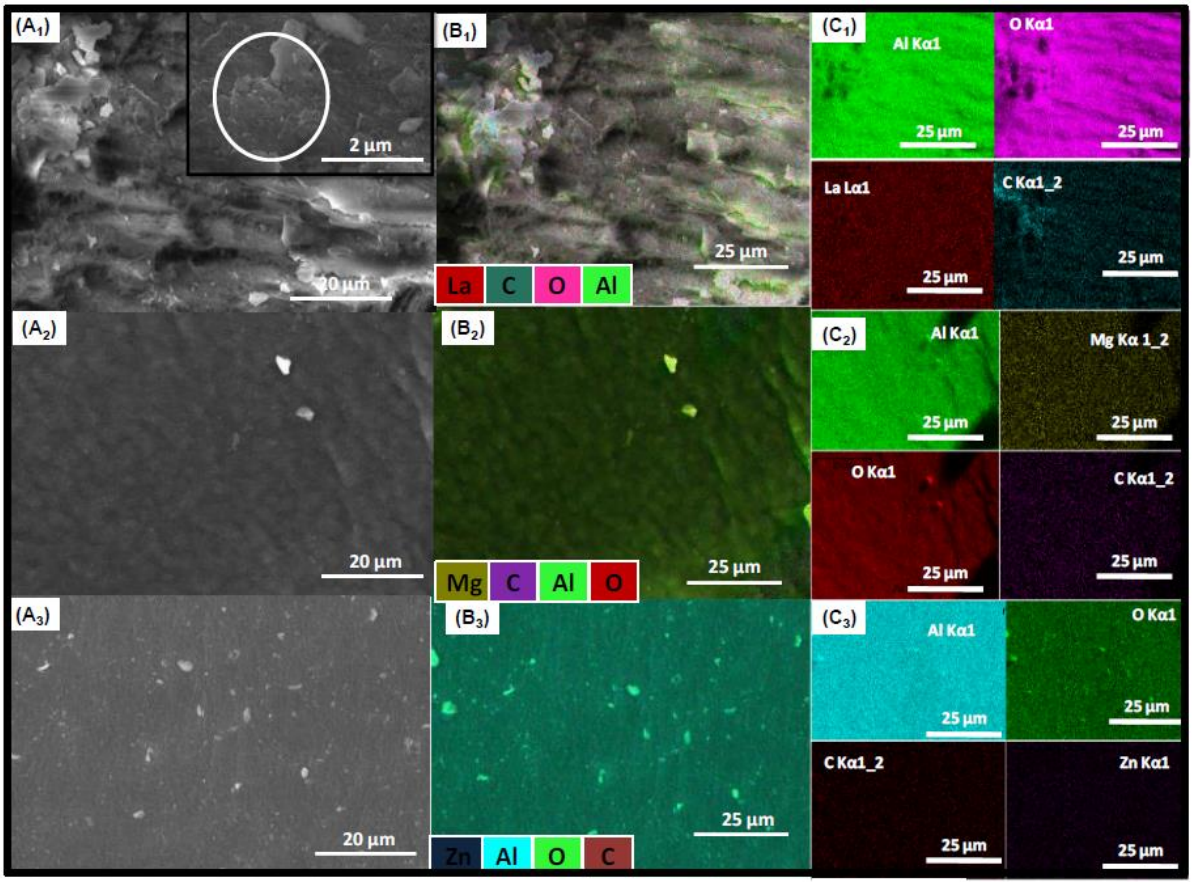


Figure S1. (A) SEM images, (B) EDS images and (C) EDS mapping of the unsupported solids. The numbers 1, 2 and 3 at the right side of the letters represent the LA, MA and ZA samples.

On the contrary, the MA sample has a minor amount of Mg on the surface, e.g., 1.7%, while the O, Al and C amounts are within 51.4, 40.4, and 1.1%, respectively (Figure S1B$_2$). This means that Al and Mg are not well distributed on the surface (Figure S1C$_2$). An enrichment of the Al element on the surface of ZA is illustrated by the amounts of Al, O, Zn and C of ca. 68.6, 28.0, 1.7 and 1.7%, respectively (Figure S1B$_3$). The presence of Zn in an inhomogeneous distribution on the surface is seen by EDS mapping (Figure S1C$_3$). In all cases, carbon appears from the support used to disperse the samples.

The supported samples have some similarities concerning their morphologies due to the consecutive calcination steps, giving a rough outer surface with aggregated particle morphology at low magnifications (Figure S2A$_1$-A$_3$ in supplementary materials). In addition, the fundamental

differences in terms of rod shaped particles that mostly appear agglomerated are illustrated at high magnifications (Figure S2A$_{1}$- A$_{3}$, insets). Regardless, consecutive steps of calcination for supported solids evidence porosity, while it results in shorter pores with the shrinkage of their diameters. In agreement, the nitrogen physisorption analyses rule out the possibility of lower textural properties for thesupported samples. Furthermore, elemental compositions of the supported samples (Figure S2B$_{1}$-B$_{3}$) reveal small amounts of Mg (0.7%), La (6.6%) and Zn (1.1%) on the solid surface with the prevalence of Al (24.4-50.3%)and O (32.8-41.0%) entities, as expected. These results are further confirmed by XPS analyses that found these species with nearby compositions on the solid surface. Interestingly, a slight change in the distribution of the elements is associated with the type of support. Although the data derived from nitrogen physisorption analysis and XRD strongly indicate that the Ni and Co species are well dispersed on the LA surface, the EDS mapping (Figure 5C$_{1}$-C$_{3}$) conclusively illustrates that Ni and Co elements are unevenly distributed throughout the surface of the supports. As an example, NiCo/LA has amounts of Co and Ni, approximately 13.7 and 19.2%, respectively. In contrast, low amounts of approximately 3.0-3.6 and 4.3-4.6% for Co and Ni, respectively, are found well-dispersed on NiCo/MA and NiCo/ZA supports, suggesting that they can rarely be imaged on the bulk of the solids. TEM measurements show similar observations.

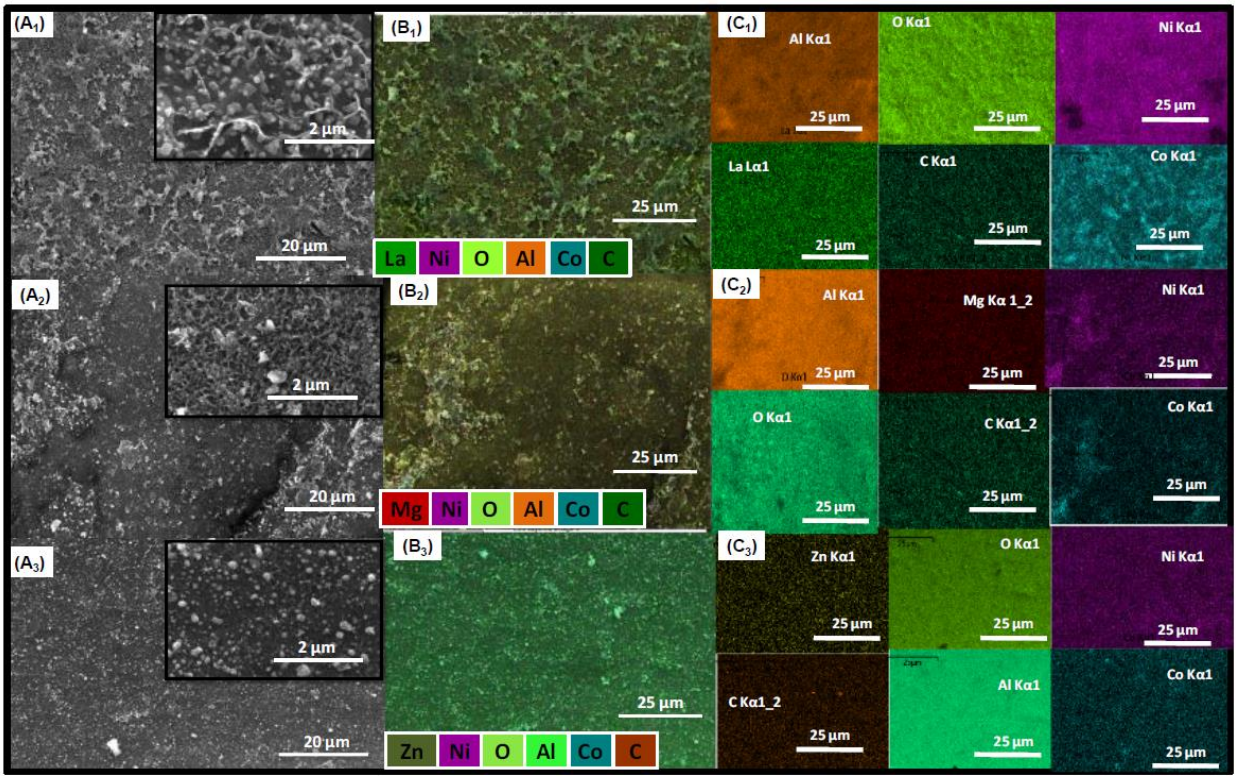
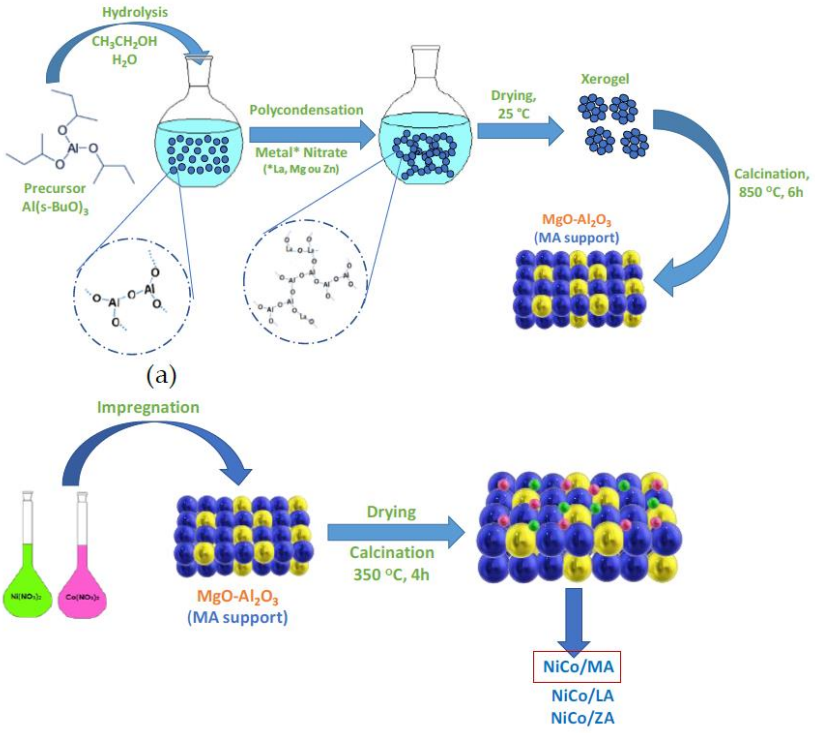


Figure S2. (A) SEM images, (B) EDS images and (C) EDS mapping of the supported solids. The numbers 1, 2 and 3 at the right side of the letters represent the LA, MA and ZA samples.

In line with these results, the composition of the solids is in correspondence with the formation of ZnO-Al$_2$O$_3$, MgO-Al$_2$O$_3$ and La$_2$O$_3$-Al$_2$O$_3$ supports being prone to disperse the active centers on the catalysts. Additionally, chemical analysis shows that the samples have limited Ni and Co amounts, distinct from the nominal samples due to the leaching and calcination process.



FigureS3. Schematic illustration of the (a) synthesis of the supports and (b) NiCo impregnation on the supports.