Ex-LDH-Based Catalysts for CO$_2$ Conversion to Methanol and Dimethyl Ether

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Abstract: CO$_2$-derived methanol and dimethyl ether can play a very important role as fuels, energy carriers, and bulk chemicals. Methanol production from CO$_2$ and renewable hydrogen is considered to be one of the most promising pathways to alleviate global warming. In turn, methanol could be subsequently dehydrated into DME; alternatively, one-step CO$_2$ conversion to DME can be obtained by hydrogenation on bifunctional catalysts. In this light, four oxide catalysts with the same Cu and Zn content (Cu/Zn molar ratio = 2) were synthesized by calcining the corresponding CuZnAl LDH systems modified with Zr and/or Ce. The fresh ex-LDH catalysts were characterized in terms of composition, texture, structure, surface acidity and basicity, and reducibility. Structural and acid-base properties were also studied on H$_2$-treated samples, on which specific metal surface area and dispersion of metallic Cu were determined as well. After in situ H$_2$ treatment, the ex-LDH systems were tested as catalysts for the hydrogenation of CO$_2$ to methanol at 250 °C and 3.0 MPa. In the same experimental conditions, CO$_2$ conversion into dimethyl ether was studied on bifunctional catalysts obtained by physically mixing the ex-LDH hydrogenation catalysts with acid ferrierite or ZSM-5 zeolites. For both processes, the effect of the Al/Zr/Ce ratio on the products distribution was investigated.

Keywords: CO$_2$ hydrogenation; methanol synthesis; DME synthesis; ex-LDH; bifunctional catalysts

1. Introduction

Clean fuel production from carbon dioxide and the excess of renewable electricity is attracting the interest of the scientific and industrial community [1] since it allows for solving two problems at the same time: first of all, it allows for storing the overproduction of electricity in chemical form [2], with the subsequent stabilization of the electrical grid, and promoting a further exploitation of renewable sources [3]; in parallel, it uses carbon dioxide as a feedstock, generating a circular economy based on carbon, seen as a resource instead of a problem [4,5]. This approach is not limited to the power generation sector, but can also be applied to several kinds of industrial plants (steel and cement in particular) [6].

In this scenario, CO$_2$-derived methanol and dimethyl ether (DME) can play a very important role as e-fuels (commonly defined as fuels produced using renewable energy), energy carriers, and building blocks in the chemical industry [7].

Methanol is commonly produced from syngas using commercial CuO/ZnO/Al$_2$O$_3$ catalysts [8]. However, its production from CO$_2$ and renewable hydrogen is now considered as one of the most promising pathways to alleviate the global warming and result in production of renewable fuels and valuable chemicals [9].
DME can be synthesized from CO$_2$ via two sequential steps: catalytic hydrogenation of CO$_2$ to methanol and methanol dehydration to DME. However, the severe limitations of thermodynamic equilibrium in methanol synthesis are the bottleneck of this process. To overcome this drawback, the one-step hydrogenation of CO$_2$ to DME over a bifunctional catalyst can be considered as a near-term perspective process. In the synthesis of DME from CO$_2$, three main reactions take place:

1. \[ \text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H = -49.4 \text{ kJ mol}^{-1} \quad \text{(methanol synthesis)} \]
2. \[ 2 \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \quad \Delta H = -23.4 \text{ kJ mol}^{-1} \quad \text{(methanol dehydration)} \]
3. \[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad \Delta H = +41.2 \text{ kJ mol}^{-1} \quad \text{(reverse water gas shift)} \]

Catalysts for the direct CO$_2$-to-DME process should be able to efficiently catalyze both methanol synthesis and methanol dehydration reactions, while the yield to CO$_2$ formed via the reverse water gas shift side reaction, should be kept to a minimum.

Besides the conventional CuO/ZnO/Al$_2$O$_3$, different Cu-based catalytic systems have been investigated for the methanol synthesis from CO$_2$ [10–13]. Among them, the ZrO$_2$-containing catalysts have been recently claimed to be very active and selective due to the versatile properties and weak hydrophilic character of zirconia [12].

On the other hand, methanol dehydration reaction takes place rapidly over a solid acid component. Thus, due to the high activity and easy preparation of the Cu-ZnO-based systems, bifunctional catalysts for directly converting CO$_2$ into DME can be obtained by combining such redox systems with solid acid catalysts [14], among which H-ZSM-5 [8,15–22], ferrierite [17,19,20,23,24], mordenite [17,19,20], and γ-Al$_2$O$_3$ [25,26].

Particle size, surface area, metallic Cu$^\circ$ surface area, and composition of the catalyst are important factors that affect catalytic performance; in turn, they are influenced by the catalyst synthesis method. Preparation methods usually involve the co-precipitation of the metal precursors from the liquid phase through sodium carbonate and the subsequent aging step for the formation of crystalline hydroxycarbonate precursors [27,28]. By using a well-controlled co-precipitation method, a Cu/Zn/Al/Zr catalytic system with excellent performance for CO$_2$ hydrogenation to methanol can be obtained [29,30]. As a result, considerable attention has been recently paid to hydrotalcite-like compounds as catalyst precursors with the general formula of $\left[M^{n+}\cdot M^{n+}\cdot (\text{OH})\right]^{m+}(\text{A}^{m-})_{n}\cdot m\text{H}_2\text{O}$. Such layered double hydroxide (LDH) materials are characterized by a homogeneous dispersion of metal cations at an atomic level, high stability against sintering, high specific surface area, and appropriate basic properties [31,32]. However, to the best of the authors’ knowledge, very few papers dealing with the use of redox catalysts obtained by calcination of LDH systems (ex-LDH) for the CO$_2$ hydrogenation to dimethyl ether have been published so far. This ex-LDH system is peculiar, probably associated to the coordination requirements of Cu$^{2+}$ to form distorted octahedra, introducing the Jahn–Teller effect into the layers and, thereby, destabilizing the hydrotalcite-like structure [30,33]. Therefore, this work aims to probe the ex-LDH compounds for the preparation of ternary and multicomponent redox catalysts for the methanol synthesis and the physical mixture with different acidic catalysts for the CO$_2$ hydrogenation to dimethyl ether.

2. Results and Discussion

2.1. Characterization of As-Prepared Ex-LDH Catalysts

The chemical composition of the mixed oxides obtained by calcination of the LDH systems is reported in Table 1, in terms of both metal molar ratios and weight percentages of the oxides. It can be observed that the experimental values of the molar ratios are comparable with the nominal ones for all the catalysts and that the CuZnAl sample shows a notably higher amount of copper oxide.
Table 1. Chemical composition of the as-prepared ex-LDH catalysts determined by ICP-AES.

| Sample       | Molar Ratio Cu/Zn/Al/Zr/Ce | Composition (wt%) |
|--------------|----------------------------|-------------------|
|              |                            | CuO  | ZnO  | Al₂O₃ | ZrO₂ | CeO₂ |
| CuZnAl       | 2.1/1.0/0.98 (nominal: 2/1/1) | 56   | 27   | 17    | -    | -    |
| CuZnAlZr     | 2.0/1.0/0.8/0.24 (nominal: 2/1/0.7/0.3) | 51   | 26   | 13    | 10   | -    |
| CuZnAlCe     | 2.0/1.0/0.76/0.31 (nominal: 2/1/0.7/0.3) | 48   | 24   | 12    | -    | 16   |
| CuZnAlZrCe   | 2.0/1.0/0.76/0.13/0.16 (nominal: 2/1/0.7/0.15/0.15) | 49   | 25   | 12    | 5    | 9    |

The N₂ adsorption/desorption isotherms of the as-prepared ex-LDH samples are shown in Figure 1. All curves are of type IIb, typical for non-porous or macroporous materials, that allow unrestricted multilayer formation at high \( p/p₀ \) values [34]. The presence of narrow hysteresis loops is ascribable to the inter-particle capillary condensation. Specific surface areas (\( S_{BET} \)) and specific pore volumes (\( Vₚ \)) are summarized in Table 2. Such values are comparable to those obtained for Cu/Zn-based catalysts synthesized by the urea-nitrate combustion method [35], by co-precipitation [36], or from hydrotalcite-like precursors [37–39].

Figure 1. N₂ adsorption (full symbols)/desorption (open symbols) isotherms of the as-prepared ex-LDH catalysts: (a) CuZnAl; (b) CuZnAlZr; (c) CuZnAlCe; (d) CuZnAlZrCe.
Table 2. Textural features of the as-prepared ex-LDH catalysts.

| Sample       | \( S_{\text{BET}} \) (m\(^2\) g\(^{-1}\)) | \( V_p \) (cm\(^3\) g\(^{-1}\)) |
|--------------|------------------------------------------|----------------------------------|
| CuZnAl      | 45                                       | 0.17                             |
| CuZnAlZr    | 64                                       | 0.38                             |
| CuZnAlCe    | 49                                       | 0.39                             |
| CuZnAlZrCe  | 66                                       | 0.41                             |

The X-ray diffraction patterns of the as-prepared ex-LDH mixed oxides are reported in Figure 2. For all the samples, the most definite signals (in particular, the reflections at \( 2\theta = 35.5^\circ \) and \( 38.7^\circ \)) are ascribable to the CuO phase (PDF card 80-1917) and are clearly superimposed to wider signals, related to amorphous or highly dispersed aluminum, zinc, cerium and/or zirconium oxides. Due to such superimposition, the crystallite size calculated by the Scherrer equation in the 8–12 nm range can only be considered as a rough estimate. For CuZnAlCe, wide signals ascribable to nanocrystalline (crystallite size ca. 3 nm) cubic CeO\(_2\) are noticeable at \( 2\theta = 28.5^\circ \) and \( 47.5^\circ \) (PDF card 75-151). For CuZnAlZrCe similar signals are present, but they are shifted to higher angles, most likely due to the formation of a CeO\(_2\)-ZrO\(_2\) solid solution.

Figure 2. XRD patterns of the as-prepared ex-LDH catalysts.

The surface acidity and basicity of the ex-LDH mixed oxides were investigated by adsorption microcalorimetry of NH\(_3\) and CO\(_2\), respectively. From the combination of the data of the adsorption isotherm (quantity adsorbed as a function of pressure) and of the calorimetric isotherm (integral heat of adsorption as a function of pressure), the curves of the differential heat of adsorption \( (Q_{\text{diff}}) \) as a function of the amount of adsorbing sites \( (n) \) can be obtained, from which it is possible to get information both on the concentration of the sites and on their strength. The results are shown in Figures S1 and S2 and summarized in Table 3. \( Q_{\text{diff}} \) values of 60 and 40 kJ mol\(^{-1}\), corresponding to about three times the NH\(_3\) and CO\(_2\) condensation heats at 80 °C (20.2 and 13.7 kJ mol\(^{-1}\), respectively), have been considered as the threshold values between chemical and physical or non-specific adsorption: sites with lower adsorption heats have hence been neglected when assessing the
Table 3. Acid and base sites strength distribution for the as-prepared ex-LDH catalysts.

| Sample       | $n_A$ (μmol g$^{-1}$) | $m$ (μmol g$^{-1}$) |
|--------------|-----------------------|---------------------|
|              | $n_{A,w}$| $n_{A,m}$| $n_{A,s}$| $n_{A,bd}$| $n_{B,w}$| $n_{B,m}$| $n_{B,s}$| $n_{B,bd}$| $m_{A,w}$| $m_{B,m}$| $m_{A,s}$| $m_{B,s}$| $m_{B,bd}$| $m_{B,tot}$| $m_{B,tot}$|
| CuZnAl       | 23      | 15      | 15      | 53      | 0.2      | 0.2      | 1.8      | 2.2      |           |           |           |           |           |           |           |           |
| CuZnAlZr     | 38      | 13      | 19      | 70      | 10       | 6        | -        | 16       |           |           |           |           |           |           |           |
| CuZnAlCe     | 47      | 17      | 20      | 84      | 19       | 10       | -        | 29       |           |           |           |           |           |           |           |
| CuZnAlZrCe   | 47      | 6       | 33      | 86      | 16       | 9        | -        | 25       |           |           |           |           |           |           |           |

(a) 60 $\leq$ $Q_{diff}$ $<$ 100 kJ mol$^{-1}$; (b) 100 $\leq$ $Q_{diff}$ $<$ 150 kJ mol$^{-1}$; (c) $Q_{diff}$ $\geq$ 150 kJ mol$^{-1}$; (d) $Q_{diff}$ $\geq$ 60 kJ mol$^{-1}$.

To investigate the reducibility of the oxide catalysts, H$_2$ temperature programmed reduction analyses were carried out, and the obtained results are shown in Figure 3. As can be seen, the TPR profiles are quite complex and indicate the presence of different reducible species. According to the literature, ZnO [40], Al$_2$O$_3$ [41], and ZrO$_2$ [42] do not undergo reduction processes in the adopted operating conditions. Therefore, the reducible species are reasonably constituted by different copper species, such as highly dispersed and bulk-like CuO phases, whose reducibility might also be affected by the interactions with the other component oxides. However, in the case of the CuZnAlCe and CuZnAlZrCe samples, a minor contribution ascribable to the surface reduction process of ceria at temperatures higher than 300 °C cannot be excluded [43]. The TPR curve of CuZnAl shows three distinct peaks of hydrogen consumption, with maxima between 260 and 325 °C; such a sample appears to be the most difficult to reduce, as its reduction process starts around 170 °C ($T_{onset}$) and is complete at 350 °C. The addition of ZrO$_2$ and/or CeO$_2$ seems to positively influence the reducibility of the CuO species, as indicated by the decrease in $T_{onset}$ (< 150 °C) and in the temperatures of maximum hydrogen consumption (in the range 210–260 °C). These results are in agreement with those reported in the literature [44], where a shift of the reduction peaks towards higher temperatures was observed after addition of alumina to a CuO-ZnO reference sample and ascribed to the strong interactions between Al$_2$O$_3$ and CuO; conversely, the further addition of ZrO$_2$ to the catalyst formulation was found to promote the reducibility of the copper oxide phase. The reduction extent for the samples, calculated by determining the amount of H$_2$
consumed in the reduction process from the area under the TPR curve and considering a Cu$^{2+}$:H$_2$ stoichiometry of 1:1, was found to be $\geq 90\%$, the lowest value being obtained for the CuZnAl sample.

Figure 3. H$_2$-TPR profiles of the as-prepared ex-LDH catalysts: (a) CuZnAl; (b) CuZnAlZr; (c) CuZnAlCe; (d) CuZnAlZrCe.

2.2. Characterization of the H$_2$-Treated Ex-LDH Catalysts

In order to investigate the effect of the H$_2$ treatment typically undergone by the catalysts prior to the catalytic tests, the ex-LDH mixed oxides were treated in H$_2$ atmosphere at 250 °C and characterized.

The XRD patterns of the H$_2$-treated ex-LDH samples are reported in Figure 4. For all the samples, besides the same wide signals already observed for the calcined samples (cf. Figure 2), reflections at $2\theta = 43.3^\circ$ and $50.4^\circ$ are present. The latter are ascribable to metallic copper (PDF card 4-836), which clearly derives from the reduction of CuO, whose signals are no more visible. Metallic copper crystallite size, calculated by the Scherrer equation, is in the range 10–13 nm.
The values of the dispersion of metallic Cu ($D_{Cu0}$) and of the metallic Cu surface area per mass of catalyst ($A_{Cu}^{cat}$) are shown in Table 4. The obtained values indicate a slightly higher copper dispersion in the CuZnAlCe and CuZnAlZrCe samples, possibly due to a lower copper content (wt%) owing to the replacement of Al$_2$O$_3$ and/or ZrO$_2$ with the heavier CeO$_2$.

Table 4. Dispersion of metallic copper and specific surface area determined on the H$_2$-treated ex-LDH catalysts by N$_2$O adsorptive decomposition at controlled temperature followed by H$_2$-TPR.

| Sample       | Cu Content (wt%) | $D_{Cu0}$ (%) | $A_{Cu}^{cat}$ (m$^2$ g$^{-1}$) |
|--------------|-----------------|---------------|-------------------------------|
| CuZnAl      | 45              | 6.4           | 19                            |
| CuZnAlZr    | 41              | 6.8           | 18                            |
| CuZnAlCe    | 38              | 8.1           | 20                            |
| CuZnAlZrCe  | 39              | 8.0           | 20                            |

(a) Calculated from ICP-AES results (cf. Table 1).

The adsorption microcalorimetry data of the H$_2$-treated samples are shown in Figures S1 and S2. The curves of $Q_{diff}$ vs. the NH$_3$ adsorbed amount still present a continuous decrease, confirming the heterogeneity of the surface acid sites from the energetic point of view (Figure S1). It can be noted that, though significantly lower than for the as-prepared samples, the initial values of $Q_{diff}$ for the H$_2$-treated ones are still higher than 150 kJ mol$^{-1}$, suggesting that a small number of strong acid sites are still present. By looking at data reported in Table 5, it can be seen that the H$_2$ treatment leads to an increase in the total number of acid sites, principally due to the increase in the number of weak sites. However, by calculating the fraction of medium and strong sites with respect to the total ones, a general decrease in the acid properties upon H$_2$ treatment can be highlighted; in fact, these sites together account for percentages in the range 44%–57% for the as-prepared oxides, which decrease to values between 29% and 38% for the samples subjected to the H$_2$ treatment (Table S1).
By looking at the curves of \(Q_{\text{diff}}\) as a function of CO\(_2\) adsorbed amount (Figure S2), it can be noted that the initial values of \(Q_{\text{diff}}\) are significantly higher than those of the as-prepared oxides, except for the CuZnAl sample. In addition, all the curves of the H\(_2\)-treated samples lie above those of the as-prepared ones, suggesting an increase in the basic surface properties. For the CuZnAlCe sample, the presence of a family of homogeneous weak base sites is also revealed by a well-defined plateau observable at ca. 70 kJ mol\(^{-1}\). Interestingly, the increase in basicity is largely due to the increase in the number of strong sites (Table 5). Except for CuZnAl (which shows a much lower amount of basic sites than the other samples in the series), the percentages of medium and strong sites increase in comparison with those of the as-prepared oxides, confirming their higher basicity after the H\(_2\) treatment.

Notably, by comparing the acidic and basic properties of the reduced catalysts, it appears that, for CuZnAl, the number of total acid sites is more than ten times greater than that of the basic ones. In the case of the other catalysts, the value of \(\frac{\text{H}_2\text{tot}}{\text{B}_\text{tot}}\) is much lower, being in the order CuZnAlZr > CuZnAlZrCe > CuZnAlCe (Table S1). In addition, in the case of the Zr- and/or Ce-containing samples also the value of \(\frac{\text{H}_2\text{tot}}{\text{B}_\text{tot}}\) is significantly lower than that of CuZnAl and is the lowest for the CuZnAlCe, pointing out the former as the most acidic catalyst and the latter as the most basic one.

Table 5. Acid and base sites strength distribution for the H\(_2\)-treated LDH samples.

| Sample        | \(\text{H}_2\) (μmol g\(^{-1}\)) | \(\text{B}_2\) (μmol g\(^{-1}\)) |
|---------------|----------------------------------|----------------------------------|
|               | \(H_{\text{A,1}}\) \((\text{a})\) | \(H_{\text{B,1}}\) \((\text{b})\) | \(H_{\text{A,2}}\) \((\text{c})\) | \(H_{\text{B,2}}\) \((\text{d})\) | \(H_{\text{A,3}}\) \((\text{e})\) | \(H_{\text{B,3}}\) \((\text{f})\) | \(H_{\text{A,4}}\) \((\text{g})\) | \(H_{\text{B,4}}\) \((\text{h})\) |
| CuZnAl        | 53                              | 17                               | 12                               | 82                             | 3                               | 1                               | 3                               | 7                               |
| CuZnAlZr      | 67                              | 23                               | 19                               | 109                            | 18                              | 3                               | 8                               | 29                              |
| CuZnAlCe      | 102                             | 29                               | 12                               | 143                            | 20                              | 13                              | 16                              | 49                              |
| CuZnAlZrCe    | 72                              | 20                               | 17                               | 109                            | 14                              | 6                               | 14                              | 34                              |

\((\text{a}) \ 60 \leq Q_{\text{diff}} < 100 \text{ kJ mol}^{-1} \); \((\text{b}) 100 \leq Q_{\text{diff}} < 150 \text{ kJ mol}^{-1} \); \((\text{c}) Q_{\text{diff}} \geq 150 \text{ kJ mol}^{-1} \); \((\text{d}) Q_{\text{diff}} \geq 60 \text{ kJ mol}^{-1} \).

\((\text{e}) 40 \leq Q_{\text{diff}} < 100 \text{ kJ mol}^{-1} \); \((\text{f}) 100 \leq Q_{\text{diff}} < 150 \text{ kJ mol}^{-1} \); \((\text{g}) Q_{\text{diff}} \geq 150 \text{ kJ mol}^{-1} \); \((\text{h}) Q_{\text{diff}} \geq 40 \text{ kJ mol}^{-1} \).

2.3. Characterization of the Zeolite Catalysts

The bifunctional catalysts used for DME synthesis were obtained by physically mixing the ex-LHD oxides with three acid zeolites (obtained by calcining the commercial ammonium form): one ferrierite with SiO\(_2\)/Al\(_2\)O\(_3\) ratio of 20:1 (FER_20) and two ZSM-5, with SiO\(_2\)/Al\(_2\)O\(_3\) molar ratios of 350:1 and 23:1 (ZSM5_350 and ZSM5_23, respectively). The surface acidity of the zeolite samples was investigated by adsorption microcalorimetry of ammonia and the curves of \(Q_{\text{diff}}\) as a function of the adsorbed amount of NH\(_3\) are shown in Figure 5. After a very high initial value (> 275 kJ mol\(^{-1}\)), indicative of the presence of a low number of very strong acid sites, the adsorption heat decreases at increasing NH\(_3\) adsorbed amount. Such a decrease is particularly fast for the ZSM5_350 sample, for which heat values typical for non-specific adsorption are achieved at extremely low ammonia adsorption. In the case of FER_20 and ZSM5_23 a quasi-plateau is observable in the range 100–150 kJ mol\(^{-1}\), which is more evident for the former catalyst and suggests the existence of energetically homogeneous sites.
Figure 5. Differential heat of adsorption of NH₃ as a function of the amount of the adsorbing sites for zeolite samples: (○), FER_20; (●), ZSM5_23; (■), ZSM5_350.

The surface acid properties are summarized in Table 6 in terms of sites strength distribution. FER_20 and ZSM5_23 show similar acid properties, both in terms of sites concentration and strength distribution, while the ZSM5_350 sample possesses a number of sites that is one order of magnitude lower than for the other two samples. This result, as well as the remarkable increase in the fraction of strong acid sites (Table 6), is expected as a consequence of dealumination.

Table 6. Acid sites strength distribution for the zeolite samples.

| Sample   | n_A (μmol g⁻¹) | n_A distribution (%) |
|----------|----------------|-----------------------|
|          | n_A,w|n_A,m|n_A,s|n_A,tot|n_A,w/n_A,tot|n_A,m/n_A,tot|n_A,s/n_A,tot|
| FER_20   | 1292 | 681 | 83  | 2056 | 63 | 33 | 4 |
| ZSM5_23  | 1293 | 555 | 56  | 1904 | 68 | 29 | 3 |
| ZSM_350  | 96  | 45  | 33  | 174  | 55 | 26 | 19 |

(a) 60 ≤ Qdiff < 100 kJ mol⁻¹; (b) 100 ≤ Qdiff < 150 kJ mol⁻¹; (c) Qdiff ≥ 150 kJ mol⁻¹; (d) Qdiff ≥ 60 kJ mol⁻¹.

2.4. Catalytic Results for CO₂ Conversion to Methanol

The ex-LDH oxide samples were tested as catalysts for the CO₂ hydrogenation to methanol in 24-hour runs. CO₂ conversion (XCO₂) as a function of time on stream are reported in Figure S3. Very similar and almost constant XCO₂ values were obtained for all samples with the exception of CuZnAlCe, for which conversion is somewhat lower and slightly decreasing with time on stream. Average values (over 24 hours on stream) of CO₂ conversion (XCO₂), selectivity to different products (S), as well as methanol yield (YCH₃OH) and space time yield (STYCH₃OH), are reported in Table 7 and Figure S4. Under the conditions of the catalytic tests, the main products of CO₂ hydrogenation were methanol and carbon monoxide, water being coproduced in both reactions. Light hydrocarbons (methane, ethane, and propane) were also monitored during the reaction and detected in very low amounts.
Catalysts 2021, 11, 615

Table 7. Catalytic results (average values over 24 hours on stream) for CO₂ hydrogenation to methanol on ex-LDH oxides. Reaction conditions: \( T = 250 \degree C; P = 3.0 \text{MPa}; H_{2}/CO_{2} = 3 \text{ mol mol}^{-1} \); \( GHSV = 12000 \text{Ncm}^{3} \text{g}_{\text{cat}}^{-1} \text{h}^{-1} \).

| Catalyst    | \( X_{\text{CO}_2} \) (mol%) | \( S_{\text{CO}} \) (mol%) | \( S_{\text{CH}_3\text{OH}} \) (mol%) | \( S_{\text{DME}} \) (mol%) | \( S_{\text{CH}_3\text{H}_2\text{O}} \) (mol%) | \( Y_{\text{CH}_3\text{OH}} \) (mol%) | \( \text{STY}_{\text{CH}_3\text{OH}} \) (mg\text{CH}_3\text{OH} g_{\text{cat}}^{-1} \text{h}^{-1}) |
|-------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|--------------------------------|
| CuZnAl      | 18.6                        | 65.3                        | 27.7                        | 6.9                         | 0.1                         | 5.2                         | 205                           |
| CuZnAlZr    | 18.7                        | 66.3                        | 33.7                        | traces                      | traces                      | 6.3                         | 250                           |
| CuZnAlCe    | 14.2                        | 61.6                        | 37.8                        | 0.6                         | traces                      | 5.4                         | 213                           |
| CuZnAlZrCe  | 17.9                        | 64.7                        | 32.5                        | 2.6                         | 0.2                         | 5.8                         | 230                           |

The non-negligible value of the DME selectivity for the CuZnAl catalyst can be reasonably explained by considering its surface acid–base properties, which highlight the definite predominance of acidic sites compared to basic ones (cf. Tables 5 and S1).

As expected, the catalytic performance is affected by the presence of zirconium and/or cerium. The partial substitution of aluminum with zirconium in the CuZnAlZr catalyst, while retaining the same conversion of the CuZnAl catalyst despite the lower Cu content, enhances the selectivity to methanol at the expense of the formed amount of DME, thus leading to a manifest increase in the productivity of methanol (Table 7). Though the synergistic effects induced by ZrO₂ have been extensively investigated, its multiple roles in the catalytic process are still under debate. ZrO₂ is known to enhance the Cu/Zn dispersion and the redox properties of the Cu species [12]. In the present case, the positive effect of Zr addition on the textural properties of CuZnAlZr in comparison with CuZnAl is proved by the increase in the \( S_{\text{BET}} \) and \( V_{p} \) values (cf. Table 2); conversely, no appreciable differences are observed between the two catalysts with regard to dispersion and specific surface area of Cu (cf. Table S1). Thus, the improvement of the catalytic performance in terms of \( \text{STY}_{\text{CH}_3\text{OH}} \) is reasonably ascribable to the changes in the acid-base properties, in that the decrease in DME formation would be due to the remarkable decrease in the \( n_{\text{A,(Al)}}/n_{\text{B,(Al)}} \) ratio (cf. Table S1). Notably, the present CuZnAlZr catalyst shows better performance than a similar sample (CHT-Al0.9 in [38]), which—despite the higher Cu dispersion and the higher operating pressure—presented a lower space time yield (0.19 g\text{CH}_3\text{OH} g_{\text{cat}}^{-1} \text{h}^{-1}). In fact, the main difference in the composition of the two systems is the higher Zr content in the present CuZnAlZr sample, which is in line with the already observed beneficial effect of zirconium.

For the CuZnAlCe catalyst, where Zr is completely replaced by cerium, a lower conversion in the presence of ceria was already observed for CuZnAlCe catalysts (M = Al, Ce, Ce-Zr) [46] and were ascribed to its lower efficiency in improving the textural properties and metal surface area of the catalyst in comparison with zirconia. On the other hand, the increase in methanol selectivity was attributed to the promoting effect of ceria in adsorbing and activating the CO₂ molecule. For M-promoted CuZnAl catalysts (M = Mn, La, Ce, Zr, Y), the selectivity to CH₃OH was found to be correlated with the increase in the strength of the surface basic sites, which were classified as weak (α), moderate (β), and strong (γ) ones by temperature programmed desorption of CO₂ [47]. It was proposed that CO₂ is adsorbed on the basic sites in different forms depending on their strength: bicarbonates species, which easily desorb without giving rise to the reductive event, arise from the interaction with the α sites, whereas carbonate intermediates are formed on stronger sites and can be hydrogenated by hydrogen activated on the Cu sites. Formaldehyde was proposed as a common intermediate, which can lead to the formation of CH₃OH or CO depending on whether it is adsorbed on γ or β basic sites, respectively. According
to the literature, the enhanced value of CH$_3$OH selectivity shown by the CuZnAlCe catalyst can hence be explained in light of its higher basic character. Concerning CO$_2$ conversion and methanol space–time yield, no significant differences are observed in the $A_{\text{cat}}^{\text{cat}}$ values between CuZnAlZr and CuZnAlCe (cf. Table 4), although the latter has a lower $S_{\text{Her}}$ (cf. Table 2); therefore, the worsening of its catalytic activity might tentatively be explained by an unbalanced ratio between the Cu and the basic sites responsible for the activation of H$_2$ and CO$_2$, respectively.

The partial substitution of Zr with Ce in the CuZnAlZrCe catalyst does not improve either CO$_2$ conversion or methanol selectivity compared to CuZnAlZr; on the contrary it leads to a decrease in the $STY_{\text{CH}_3\text{OH}}$ value (cf. Table 7). The lack of a synergistic effect might be due to a non-optimal Ce/Zr molar ratio. Indeed, it was observed in the literature [48,49] that the catalytic behavior is positively affected by the simultaneous presence of Ce and Zr for Ce/Zr ratios up to 1 and worsens for higher values.

2.5. Catalytic Results for CO$_2$ Conversion to Dimethyl Ether

Some fundamental aspects are considered to play a key role for developing catalytic systems with high DME productivity: i) the stability in the presence of water should be high; ii) the formation of olefins should be avoided; iii) the acidic sites should be well distributed and of suitable strength [19,50]. A study on syngas to dimethyl ether conversion using different zeolites (Theta-1, ZSM-23, ferrierite, ZSM-5) in mixture with a commercial Cu/ZnO/Al$_2$O$_3$ redox catalyst reported a superior catalytic performance in the presence of ferrierite, which was ascribed to its topology that limits the formation of hydrocarbons owing to a preferential path for the diffusion of small reactants and products. [17].

Bifunctional catalysts were then prepared by mixing the acid ferrierite zeolite (FER_20) and the redox ex-LDH synthesized systems and tested for the direct CO$_2$ hydrogenation to DME. The two components were mixed in a 1:1 weight ratio, since it was reported as the most performing [17,51]. CO$_2$ conversion ($X_{\text{CO}_2}$) as a function of time on stream (Figure S5) showed that all the catalysts are stable within the investigated reaction time except for the bifunctional system containing CuZnAlCe, which confirms the presence of a slight deactivation, as already observed for such sample during the synthesis of methanol (cf. Figure S3). Table 8 and Figure S6 summarize the catalytic performance in terms of average values (over 24 hours on stream) of CO$_2$ conversion, selectivity to different products ($S_i$), DME yield ($Y_{\text{DME}}$) and space time yield ($STY_{\text{DME}}$). Under the employed reaction conditions, the only products of the CO$_2$ hydrogenation are DME, methanol, and carbon monoxide, water being coproduced in all the three reactions. Traces of light hydrocarbons (methane, ethane and propane) were also detected.

| Catalyst                  | $X_{\text{CO}_2}$ (mol%) | $S_{\text{CO}}$ (mol%) | $S_{\text{CH}_3\text{OH}}$ (mol%) | $S_{\text{DME}}$ (mol%) | $S_{\text{CH}_2\text{O}_2}$ (mol%) | $Y_{\text{DME}}$ (mol%) | $STY_{\text{DME}}$ (mgDME g$_{\text{cat}}^{-1}$ h$^{-1}$) |
|---------------------------|--------------------------|------------------------|---------------------------------|-------------------------|------------------------------------|-------------------------|---------------------------------|
| CuZnAl/FER_20             | 17.3                     | 61.4                   | 10.5                            | 28.1                    | -                                  | 4.9                     | 139                             |
| CuZnAlZr/FER_20           | 17.0                     | 58.7                   | 9.1                             | 32.0                    | 0.2                                | 5.4                     | 161                             |
| CuZnAlCe/FER_20           | 13.4                     | 63.0                   | 10.6                            | 26.4                    | traces                             | 3.5                     | 100                             |
| CuZnAlZrCe/FER_20         | 15.8                     | 62.4                   | 9.9                             | 27.6                    | 0.1                                | 4.4                     | 124                             |
| CuZnAlZr/ZSM5$_{23}$      | 15.4                     | 59.0                   | 9.1                             | 31.8                    | 0.1                                | 4.9                     | 140                             |
| CuZnAlCe/ZSM5$_{350}$     | 18.9                     | 56.9                   | 9.9                             | 33.2                    | traces                             | 6.3                     | 179                             |

Compared to the results obtained for the methanol synthesis (cf. Table 7) on the corresponding ex-LDH components, a decrease in CO$_2$ conversion (in the range 6%–12%) can be observed for all the catalysts; such a decrease is particularly low for the
CuZnAlCe/FER_20 sample, which, however, shows the lowest XCO₂ value. Unlike what observed for the corresponding single redox components in the CO₂ hydrogenation reaction, the CO selectivity for the CuZnAlCe/FER_20 bifunctional system is similar to that of CuZnAl/FER_20. Conversely, compared to the results previously obtained with CuZnAlZr, the CuZnAlZr/FER_20 catalyst shows an evident decrease (ca. 11%) in XCO₂, also exhibiting the highest values of DME selectivity and yields (Table 8). The superior performance of this bifunctional catalyst is in agreement with the higher methanol productivity formerly shown by the redox CuZnAlZr component (cf. Table 7).

The influence of the different zeolite framework and of the SiO₂/Al₂O₃ molar ratio was also checked. For this purpose, two more bifunctional systems were obtained by mixing the CuZnAlZr sample with two ZSM-5 zeolites having different SiO₂/Al₂O₃ ratios (ZSM5_23 and ZSM5_350). CO₂ conversion (XCO₂) as a function of time on stream, obtained on the two ZSM-5-containing bifunctional systems, is reported in Figure S7, where the results for CuZnAlZr/FER_20 are also reported for comparison. The catalytic behavior of the CuZnAlZr/FER_20 and CuZnAlZr/ZSM5_23 catalysts, where the acidic components have 2-D and 3-D pore channel systems, respectively, but similar SiO₂/Al₂O₃ molar ratios, was compared to verify the effect of the zeolite microstructure. The pertinent results, reported in Table 8 and Figure S8, show that the ZSM-5-containing catalyst performs slightly worse (10% less CO₂ converted) than the one with ferrierite, leading to lower YDME and STYDME values. Concerning the synthesis of DME from syngas [17] or from methanol in vapor phase [22] using different zeolites (1-D, 2-D, and 3-D channel structures), it was found that the 2-D porous system of ferrierite ensures a high resistance to deactivation by inhibiting the deposition of coke. However, in the present case, no deactivation occurs within the investigated time on stream (Figure S7), the better performance of the CuZnAlZr/FER_20 catalyst being possibly related to its somewhat higher number of medium and strong acid sites.

It is well known that for reactions in which water participates as a reactant or as a product, a drawback in using solid acids is the poisoning of acid sites by water; therefore, the use of water-tolerant catalysts should allow better results in terms of activity and stability. Indeed, due to the hydrophobic character of the surface, which increases with the increase in the Si/Al ratio, high-silica zeolites were found to be very efficient in the case of esterification reactions [52]. In the present case, by comparing the same ZSM-5 structure with different SiO₂/Al₂O₃ molar ratios (Table 8), it appears that the CuZnAlZr/ZSM5_350 catalyst, which contains the high-silica zeolite, shows a better catalytic activity, with YDME and STYDME values higher by approximately 29% in comparison with CuZnAlZr/ZSM5_23. According to reference [52], this result can be explained taking into account the hydrophobic character of the ZSM5_350 surface, which would favor the adsorption of methanol instead of water, favoring its transformation into DME, provided that the number of the available acid sites is sufficient.

3. Materials and Methods

3.1. Materials

All the chemicals (analytical grade), used as received without any further purification, were purchased from Sigma-Aldrich (St. Louis, Missouri, MI, USA).

3.2. Preparation of Catalysts

3.2.1. Preparation of Hydrogenation Catalysts for Methanol Synthesis

One CuZnAl LDH system and three modifications obtained through incorporation of Zr and/or Ce were prepared at room temperature by co-precipitation at low supersaturation [53]. The samples were synthesized with different Al/Zr/Ce molar ratios, but keeping the value of the Cu/Zn/(Al+Zr+Ce) molar ratio of 2:1:1. For a typical synthesis, two solutions were prepared, the first (100 cm³) containing the desired precursor metal nitrates...
in appropriate amounts (total cation concentration equal to 1.5 M) and the second obtained by dissolving 13.95 g of NaOH and 7.15 g of Na₂CO₃ in 100 cm³ of distilled water. The two solutions were then mixed under stirring, adjusting the flow rates in order to keep the pH constant (pH = 11). The final suspension was aged under stirring at 60 °C for 20 h and then cooled down to room temperature. The precipitate was filtered off, repeatedly washed with distilled water, and dried in oven at 80 °C overnight. The LDH systems were finally calcined at 500 °C for 4 h to obtain the corresponding mixed oxide catalysts (ex-LDH).

3.2.2. Preparation of Bifunctional Catalysts for DME Synthesis

Commercial zeolites were used to prepare physical mixtures with the aforementioned ex-LDH redox catalysts. One ferrierite (SiO₂/Al₂O₃ = 20:1, surface area = 400 m² g⁻¹) and two ZSM-5 (with SiO₂/Al₂O₃ molar ratios of 23:1 and 350:1 and surface areas of 425 m² g⁻¹ and 400 m² g⁻¹, respectively) zeolites were purchased from Alfa Aesar (Kandel, Germany) in the ammonium form. The zeolites were transformed into the protonic form by calcination at 550 °C for 5 h (heating rate, 3 °C min⁻¹).

3.3. Characterization of Catalysts

The chemical composition of the ex-LDH mixed oxides was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Samples (ca. 0.015 g) were dissolved in 2 cm³ of a mixture of HCl (37%) and HNO₃ (70%) (3:1 by volume). After 24 h, the solutions were diluted to 250 cm³ with Milli-Q water and analyzed with a Liberty 200 spectrophotometer (Varian, Palo Alto, California, CA, USA).

Textural analyses were performed on a Sorptomatic 1990 System (Fisons Instrument, Glasgow, UK) by determining the nitrogen adsorption/desorption isotherms at −196 °C. Prior to the analysis, the samples were heated overnight under vacuum up to 220 °C (heating rate 1 °C min⁻¹). The Brunauer–Emmett–Teller (BET) specific surface area and the specific pore volume were assessed from the adsorption data [34].

The X-ray diffraction (XRD) analysis was performed on the as-prepared and on the H₂-treated (5 vol% H₂ in N₂; flow rate, 15 cm³ min⁻¹ at 250 °C for 2 h) samples. XRD patterns were recorded on a XPert Pro diffractometer (Panalytical, Malvern, UK) with 2θ-2θ Bragg-Brentano geometry, Cu-Kα; wavelength radiation (λ = 1.54060 Å) and X'Celerator detector, operating at 40 kV and 40 mA. The crystallite size was estimated by the Scherrer equation using the Warren correction [54].

Adsorption microcalorimetry measurements were performed with a Tian–Calvet heat flow microcalorimeter (Setaram, Caluire, France), equipped with a volumetric vacuum line. Each sample (0.1 g, 40-80 mesh), as prepared or previously H₂-treated (5 vol% H₂ in N₂; flow rate, 15 cm³ min⁻¹) at 250 °C for 2 h, was thermally pretreated at 220 °C for 12 h under vacuum (5.10⁻³ Pa). Adsorption was carried out by admitting successive doses of the probe gas (NH₃ or CO₂) at 80 °C in order to limit physisorption. The equilibrium pressure relative to each adsorbed amount was measured by means of a differential pressure gauge and the thermal effect was recorded. The run was stopped at a final equilibrium pressure of about 133 Pa.

Temperature-programmed reduction (TPR) profiles were recorded on a TPD/R/O 1100 apparatus (Thermo Fisher Scientific, Waltham, Massachussets, MA, USA) under the following conditions: sample weight, 0.030 g; heating rate (from 40 to 400 °C), 10 °C min⁻¹; flow rate, 30 cm³ min⁻¹; H₂ concentration, 5 vol% in N₂. Prior to the experiment, samples were pretreated in nitrogen (20 cm³ min⁻¹) at 350 °C for 2 h. The hydrogen consumption was monitored by a thermal conductivity detector (TCD).

The copper dispersion and the specific metal surface area were evaluated by N₂O adsorptive decomposition at controlled temperature (N₂O reacts with metallic Cu on the catalyst surface to form Cu₂O and N₂), followed by H₂ temperature-programmed-reduction of the Cu₂O surface layers formed [55]. Analyses were performed on a TPD/R/O 1100
apparatus (Thermo Fisher Scientific) using the following procedure: ca. 0.1 g of fresh catalyst was first exposed to a H₂/N₂ mixture (H₂, 5 vol% in N₂; flow rate, 15 cm³ min⁻¹) at 250 °C for 2 h for reducing copper oxide to metallic copper; then, pulses of N₂O (0.347 cm³) were admitted to the sample at 40 °C using He as the gas carrier (100 cm³ min⁻¹). The oxidation of the surface metallic copper to Cu(I) was considered complete when the area of the N₂O pulses remained constant, indicating that the reactant was no longer consumed in the reaction. Finally, a H₂-TPR run (H₂, 5 vol% in N₂; flow rate, 20 cm³ min⁻¹) was performed from 40° to 400 °C (heating rate, 10 °C min⁻¹). The copper dispersion (D_{Cu}) and the Cu specific metal surface per mass of catalyst (A_{Cu}^{cat}) were calculated by the following equations:

\[
D_{Cu} = \frac{n_{H_2}^{cat} \times \alpha_{Cu/H_2} \times M_{Cu}}{W_{Cu}} \times 100 \tag{4}
\]

\[
A_{Cu}^{cat} = \frac{n_{H_2}^{cat} \times \alpha_{Cu/H_2} \times N_A}{\rho_{Cu}^{*}} \tag{5}
\]

where \(n_{H_2}^{cat}\) is the number of moles of H₂ consumed per mass of catalyst, \(\alpha_{Cu/H_2}\) is the stoichiometric ratio (\(\alpha_{Cu/H_2} = v_{Cu}/v_{H_2} = 2\) molCu molH₂⁻¹), \(M_{Cu}\) is the copper molar mass, \(W_{Cu}\) is the bulk copper content (weight fraction), \(N_A\) is the Avogadro constant (6.022 × 10²³ atoms mol⁻¹), and \(\rho_{Cu}^{*}\) is the copper surface density (1.46 × 10¹⁰ atoms m⁻²). Calibration of the H₂ amount consumed was previously carried out by using a copper oxide standard.

### 3.4. Catalytic Testing

The catalytic activity was investigated in a customized Microactivity Effi (PID Eng&Tech, Madrid, Spain) benchscale plant, employing a high-pressure fixed bed stainless steel reactor (length 304.8 mm, inner diameter 9.1 mm). A porous plate (made of Hastelloy C, 20 μm) and quartz wool were used to support the catalytic bed inside the iso-thermal temperature zone of the reactor [56,57].

For methanol synthesis experiments, the reactor was loaded with 1.00 g of catalyst, previously diluted with 2.50 g of α-Al₂O₃, in order to obtain a total bed volume of ca. 3 cm³. DME synthesis tests were performed using a physical mixture obtained combining 1.00 g of the methanol synthesis catalyst and 1.00 g of the one containing the acidic functionality; the obtained bifunctional catalytic system was diluted with 1.00 g of α-Al₂O₃ in order to reach a total bed volume of ca. 3 cm³.

Prior to catalytic tests, all fresh catalysts were reduced in situ in a stream of a H₂/N₂ mixture (H₂, 15 vol% in N₂) at 250 °C for 2 h at atmospheric pressure. Upon completion of the reduction process, the system was maintained at 250 °C, and the reaction gas mixture containing H₂ and CO₂ (molar ratio of 3:1) and 10 vol% of N₂ (used as internal standard for gas chromatographic analysis) was fed. The hydrogenation of CO₂ to methanol and DME was carried out at 3.0 MPa and gas hourly space velocity (GHSV) of 12000 and 6000 Ncm⁻³ gcat⁻¹ h⁻¹, respectively. After allowing the system to reach the steady state in 1 h on stream, analysis was periodically performed within the 24-hour runs. The reaction stream was analyzed by a 7890B (Agilent, Santa Clara, California, CA, USA) gas chromatograph equipped with a flame ionized detector (FID) for carbon-containing compounds and a thermal conductivity detector (TCD) for permanent gases. Two columns connected in series were used to identify the components of the outlet gas mixture. In particular, CO₂, methanol, dimethyl ether, ethane, and propane were separated by a HP-Plot Q (Agilent) column (length 30 m, inner diameter 0.53 mm, film thickness 40 μm), while a HP-PLOT Molesieve (Agilent) column (length 30 m, inner diameter 0.53 mm, film thickness 50 μm) was used for H₂, N₂, CH₄, and CO. To avoid condensation of condensable products, the connection lines between the plant gas outlet and gas chromatograph inlet were heated at 180 °C. CO₂ conversion (X_{CO₂}), products selectivity (S_p, with P: CH₃OH, DME, or CO), and products yield (Y_p, with P: CH₃OH or DME), were calculated as follows:
\[
X_{\text{CO}_2} = \frac{n_{\text{in}} - n_{\text{out}}}{n_{\text{in}}} \times 100 
\]

\[
S_P = \frac{\nu_{\text{CO}_2}}{v_p} \times \frac{n_{\text{in}}}{n_{\text{in}} - n_{\text{out}}} \times 100 
\]

\[
Y_P = \frac{\nu_{\text{CO}_2}}{v_p} \times \frac{n_{\text{in}}}{n_{\text{in}}} \times 100 
\]

where \( n_{\text{in}} \) and \( n_{\text{out}} \) are the number of moles of the \( i \)-th species in the feed or in the gas mixture exiting from the reactor, respectively, and \( \nu \) is the stoichiometric coefficient of the \( i \)-th species in the corresponding balanced equation.

The space–time yield of methanol and DME (STY\(_P\), with \( P: \text{CH}_3\text{OH} \) or DME), i.e., the amount of product formed per gram of catalyst per hour (mg\(_P\) g\(_{\text{cat}}\) h\(^{-1}\)) was determined by the formula:

\[
\text{STY}_P = \frac{Y_P \times \phi_{\text{CO}_2} \times M_P}{m_{\text{cat}}} \times 1000
\]

where \( Y \) is the product yield, \( \phi_{\text{CO}_2} \) is the inlet \( \text{CO}_2 \) molar flow rate (mol h\(^{-1}\)), \( M_P \) is the product molar mass (g mol\(^{-1}\)), and \( m_{\text{cat}} \) is the catalyst mass (g). Each catalytic run was performed three times with standard deviations in the range 2%–5% for both conversion and selectivity.

4. Conclusions

Four oxide catalysts with the same Cu and Zn content (Cu/Zn = 2 mol/mol) were obtained by calcining the corresponding CuZnAl LDH systems, also modified with Zr and/or Ce. The ex-LDH oxides were tested, after in situ \( \text{H}_2 \) treatment, as catalysts for the hydrogenation of \( \text{CO}_2 \) to methanol. The presence of Zr showed a beneficial effect, which could be related to the influence on the acid-base properties, assessed by means of adsorption microcalorimetry. The observation of a positive effect of zirconium was supported by the superior catalytic performance showed by the CuZnAlZr system with respect to a similar catalyst, reported in the literature, characterized by a lower Zr content.

By mixing the CuZnAlZr redox catalyst with a ferrierite zeolite, a good bifunctional system for the one-step \( \text{CO}_2 \) conversion into DME was also obtained, further confirming the favorable influence of Zr on the catalytic performance. Comparing two catalysts containing ZSM-5 zeolites with different Si/Al ratio revealed that, besides the acid–base properties, the surface hydrophobicity also significantly affects DME formation.

Supplementary Materials: The following are available online at www.mdpi.com/2073-4344/11/5/615/s1, Figure S1: Differential heat of adsorption of NH\(_3\) as a function of the amount of adsorbing sites for the ex-LDH samples, Figure S2: Differential heat of adsorption of \( \text{CO}_2 \) as a function of the amount of adsorbing sites for the ex-LDH samples, Table S1: Percentage of sites of different strength with respect to the total number and \( n_{\text{in}}/m_0 \) ratios for the mixed oxides catalysts as-prepared and after \( \text{H}_2 \) treatment, Figure S3: \( \text{CO}_2 \) conversion as a function of time on stream for the \( \text{CO}_2 \) hydrogenation to methanol on the ex-LDH catalysts, Figure S4: Catalytic results for \( \text{CO}_2 \) hydrogenation to methanol on ex-LDH oxides, Figure S5: \( \text{CO}_2 \) conversion as a function of time on stream for the \( \text{CO}_2 \) conversion into DME on the ex-LDH/FER\(_{20}\) bifunctional catalysts, Figure S6: Catalytic results for \( \text{CO}_2 \) hydrogenation to DME on ex-LDH/FER\(_{20}\) bifunctional systems, Figure S7: \( \text{CO}_2 \) conversion as a function of time on stream for the \( \text{CO}_2 \) conversion into DME on the CuZnAlZr/FER\(_{20}\) and CuZnAlZr/ZSM5 bifunctional catalysts, Figure S8: Catalytic results for \( \text{CO}_2 \) hydrogenation to DME on the CuZnAlZr/FER\(_{20}\) and CuZnAlZr/ZSM5 bifunctional systems.

Author Contributions: Conceptualization, E.R. and F.F.; methodology, M.M. and L.A.; validation, M.M., S.L., L.A., E.R., F.F. and M.G.C.; formal analysis, M.M., S.L., L.A., E.R., F.F. and M.G.C.; investigation, M.M., S.L., L.A., E.R. and M.G.C.; resources, E.R., F.F., A.P. and M.G.C.; data curation,
M.M., S.L., L.A., E.R., F.F. and M.G.C.; writing—original draft preparation, M.M., S.L., L.A., E.R., F.F., A.P. and M.G.C.; writing—review and editing, M.M., S.L., L.A., E.R., F.F., A.P. and M.G.C.; visualization, M.M., S.L., L.A., E.R. and M.G.C.; supervision, E.R., F.F. and A.P.; project administration, E.R. and F.F.; funding acquisition, A.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Regione Autonoma della Sardegna, through Sardegna Ricerche, CUP: D49J21001310002, research project “Centre of Excellence on Clean Energy project”.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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