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CuCoMgAlO$_x$ Mixed Oxides as Selective Catalysts for the Hydrogenation of Furan Compounds

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Abstract: Single phase CuCoMgAl-layered hydroxides were obtained by making fine adjustment to their composition through changing the (Co + Cu)/Mg = 0.5; 1; 2; 3 and Co/Cu = 0.5; 1; 2 ratios. The rise of Co/Cu in systems contributed to the increase in their thermal stability. CuCoMgAl-catalysts showed high selectivity of carbonyl group hydrogenation in furfural and 5-hydroxymethylfurfural. In furfural hydrogenation, the selectivity to furfuryl alcohol was more than 99%, and in 5-hydroxymethylfurfural hydrogenation, the selectivity to 2,5-hydroxymethyl furfural was 95%. The surface of the samples with different Co/Cu after calcination and reduction was the same and had a «core-shell» structure (TEM). «Core» consisted of Cu and Co metallic particles. «Shell» consisted of CuCoMgAlO$_x$ mixed no-stoichiometric spinel oxides. There was no sintering or change in size of the metallic particles after the reaction. For the sample with Co/Cu = 1, their phase composition after reaction remained unchangeable. The increase of Co/Cu led to the formation of an X-ray amorphous phase after the reaction. This suggests the decrease in structural stability of this sample. The obtained results prove the prospects of using bimetallic CoCu-systems for hydrogenation of furan aldehydes, and opens up new directions for further research and improvement.

Keywords: furfural; 5-hydroxymethylfurfural; cobalt; copper; layered hydroxides; mixed oxides

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1. Introduction

Biomass is a valuable and inexhaustible resource. Value-added chemical compounds and high-octane fuel additives can be obtained from biomass. Furfural (FAL) and 5-Hydroxymethylfurfural (5-HMF) are two of the most important components derived from biomass. These platform molecules are promising starting compounds for obtaining a variety of value-added products through the catalytic hydrogenation of FAL and 5-HMF [1]. This is possible due to the presence of the reactive functional groups -CHO and -CH$_2$OH in the structure of the platform molecules.

Furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFOL), 2-methylfuran (2-MF), and 2-methyltetrahydrofuran (2-MTHF) are obtained in the reaction of FAL selective hydrogenation. These valuable compounds are widely used to produce resins, plastics, synthetic fibers, and various protective coatings [2]. 2,5-dihydroxymethyl furfural (DHMFAL) and 2,5-dihydroxy methyltetrahydrofurfural (DHMTHFAL) can be obtained from 5-HMF through hydrogenation. These compounds are used as monomers and solvents [3,4]. 2,5-dimethylfuran (DMF) is also obtained through the hydrogenation of 5-HMF, and is an important component of biofuels [5,6].

Copper-chromium oxide catalysts currently used in industry for the hydrogenation of furfural are toxic [7,8]. Catalysts containing noble metals Ru [9,10], Pd [11–13], and Pt [14] deposited on various supports exhibit high activity during FAL and 5-HMF hydrogenation. However, the high cost of such catalysts limits their widespread use. This initiates the search for new, non-toxic, and cheap systems that are not inferior in their catalytic characteristics to the listed catalysts.

Cu- and Co-containing monometallic catalysts are widely known for their hydrogenating properties, high activity, and low cost [15]. However, there is a significant sintering of metal particles during the reaction in these systems, along with high activity. This ultimately has a detrimental effect on the stability of the catalysts [7].

In this regard, special attention is paid to the development of bimetallic catalysts. This is due to the possible occurrence of a synergistic effect between hydrogenating metals. This effect contributes to the formation of new structures with properties different from those of individual metals. As a result, the metal catalyst particles not only have optimal dimensions, but also a chemical composition in which they are characterized by stability and the best catalytic properties [16–18].

The synergistic effect of Cu and Co deposited on mesoporous silicon oxide in the hydrogenation reaction of FAL is recognized in the literature. The FAL conversion did not exceed 36.6%, with a FOL selectivity of no more than 23.3% for the monometallic catalysts. The bimetallic catalyst made it possible to achieve a FOL selectivity of about 38.1% with full FAL conversion. The reduced Cu and Co metallic nanoparticles were active sites for these catalysts. The furan and 2-MF formations were also characteristic of these systems [19]. The 5-HMF hydrogenation process on the Cu-Co catalysts supported on the carbon material was studied. The 5-HMF conversion for the Cu@C and Co@ monometallic catalysts was 70% and 100%, respectively, with DMF selectivity of 10.8 and 91.9, respectively. For the bimetallic CuCo@C catalyst, the DMF selectivity achieved 99.1% with full conversion of 5-HMF. This was due to uniformly distributed nanoparticles containing Cu and Co with zero valence [20]. Therefore, the uniform distribution of the reduced nanoparticles of catalytically active metals is an important factor in the creation of bimetallic catalysts.

The introduction of Cu and Co into the structures of hydrotalcite-like compounds is one of the ways to achieve uniform distribution at the atomic level. Hydrotalcites (layered double hydroxides, LDHs) are a class of inorganic compounds with a general formula $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2][A_{x/n}]^{n-}\cdot mH_2O$, where M^{2+} and M^{3+} are two- and three-valence metallic ions, and A^{n-} is an interlayer anion [21]. The addition of Mg to the composition of materials contributes to a more uniform distribution of catalytically active metals in the finished catalyst. This makes it possible to more finely regulate their physicochemical and catalytic properties, reduces the acidity of the surface and, accordingly, reduces the coking ability and the deactivation of catalysts caused by it [22]. The creation of CoCuMgAl-catalysts based on hydrotalcite-like compounds will allow for a one-stage catalyst synthesis excluding the anchoring of active metal on the support surface [23,24].

The aim of this work was the study of the effect of the composition of CuCo-containing catalysts based a LDH structure (Co/Cu and (Co + Cu)/Mg molar ratio) on physicochemical properties of obtained hydroxide and oxide phases, the active metals' reduction and catalytic properties of corresponding systems in FAL and 5-HMF hydrogenation with the use of water and ethanol as a solvent.

2. Materials and Methods

2.1. Catalysts Preparation

The synthesis of CuCoMgAl-layered hydroxides was carried out by coprecipitation. A water solution containing a mixture of $Cu(NO_3)_2$, $Mg(NO_3)_2$, $Co(NO_3)_2$, and $Al(NO_3)_3$ (CCu + Co + Mg + Al = 1 mol/L) was gradually added to a Na_2CO_3 solution (1 mol/L) at a constant temperature of 60 °C and a pH = 9.5 [25]. Aging was carried out at 60 °C for 18 h. Then, washing, filtration, and drying were performed at 80 °C for 18 h. $CuCoMgAlO_x$ mixed oxides were obtained by the calcination of CuCoMgAl-layered hydroxides at 550 °C for 3 h. The reduction of $CuCoMgAlO_x$ samples was carried out in a hydrogen flow at 800 °C for 2 h. The ratio of introduced magnesium was (Co + Cu)/Mg = 0.5; 1; 2; and 3. The ratio of catalytically active metals was Co/Cu = 0.5; 1; and 2. The M^{2+}/Al molar ratio in obtained catalysts was 2.

2.2. Physicochemical Characterization of the Samples

The structural properties of as-prepared CuCoMgAl-layered hydroxides, final catalysts (after oxidation and reduction stages), and catalysts after the reaction were studied by X-ray diffraction analysis (XRD). X-ray diffraction studies were carried out on a D8 Advance (Bruker, Billerica, MA, USA) diffractometer, using a Cu-Kα source in the 2θ angular range from 5° to 80°. The scanning step was 0.02°, and the signal integration time was 5 s/step. The phase composition of samples was identified using the international diffraction database ICDD PDF-2.

Thermal analysis (TG/DTA and DTG) was carried out using a DTG-60 (Shimadzu, Kyoto, Japan) instrument in the atmosphere from room temperature to 700 °C, at a heating rate of 10 °C/min.

The temperature-programmed reduction (TPR) was performed using an AutoChem II 2920 (Micromeritics, Norcross, GA, USA) chemisorption analyzer equipped with a thermal conductivity detector (TCD). The H_2-TPR experiments were carried out using a mixture of 10 vol.% H_2 and argon (flow rate of 30 m^3/min) in a temperature range of 30–800 °C, at a heating rate of 10 °C/min.

The transmission electron microscopy (TEM) images were obtained using a JEM-2100 electron microscope (JEOL Ltd., Tokyo, Japan) equipped with an energy dispersive X-ray spectrometer (INCA-250 «Oxford Instruments»). The analysis and computer processing of electron microscopic images were performed using the Digital Micrograph "Gatan" program.

2.3. Catalyst Testing

The catalytic properties of obtained samples were tested in a hydrogenation of FAL and 5-HMF. Before this, the reaction catalysts were in calcination at 550 °C for 3 h, and in reduction in a hydrogen flow at 800 °C for 2 h.

The catalyst (500 mg) was placed in a steel autoclave with a capacity of 180 mL together with a 5% wt. solution of a substrate in a solvent. The autoclave volume was cleaned of air components by blowing argon, and then hydrogen, at an atmospheric pressure. The reaction mixture was heated to a reaction temperature by circulating heated water through an external "jacket". The hydrogenation of FAL and 5-HMF was carried out at a temperature of 90 °C, and a pressure of 2.0 MPa, with stirring at 1400 rpm. The reaction was controlled by measuring the volume of consumed hydrogen with a mass flow meter EL-FLOW Select (Bronkhorst High-Tech, Netherlands).

After the completion of the reaction and cooling, the liquid phase was separated from the catalyst by filtering. The quantitative determination of the reaction products was carried out by gas chromatography HP 5890 (Agilent Technologies Inc., Santa Clara, CA, USA) in a capillary column HP-1 (100 m × 0.25 mm), and a flame ionization detector.

The *FAL* conversion X (mol.%), selectivity to each *product* S (mol.%), and *product* yield Y (mol.%) were calculated as follows:

$$X = \frac{moles\ of\ reacted\ FAL}{moles\ of\ initial\ FAL} * 100\%, \tag{1}$$

$$S_i = \frac{moles\ of\ product\ obtained}{moles\ of\ reacted\ FAL} * 100\%, \tag{2}$$

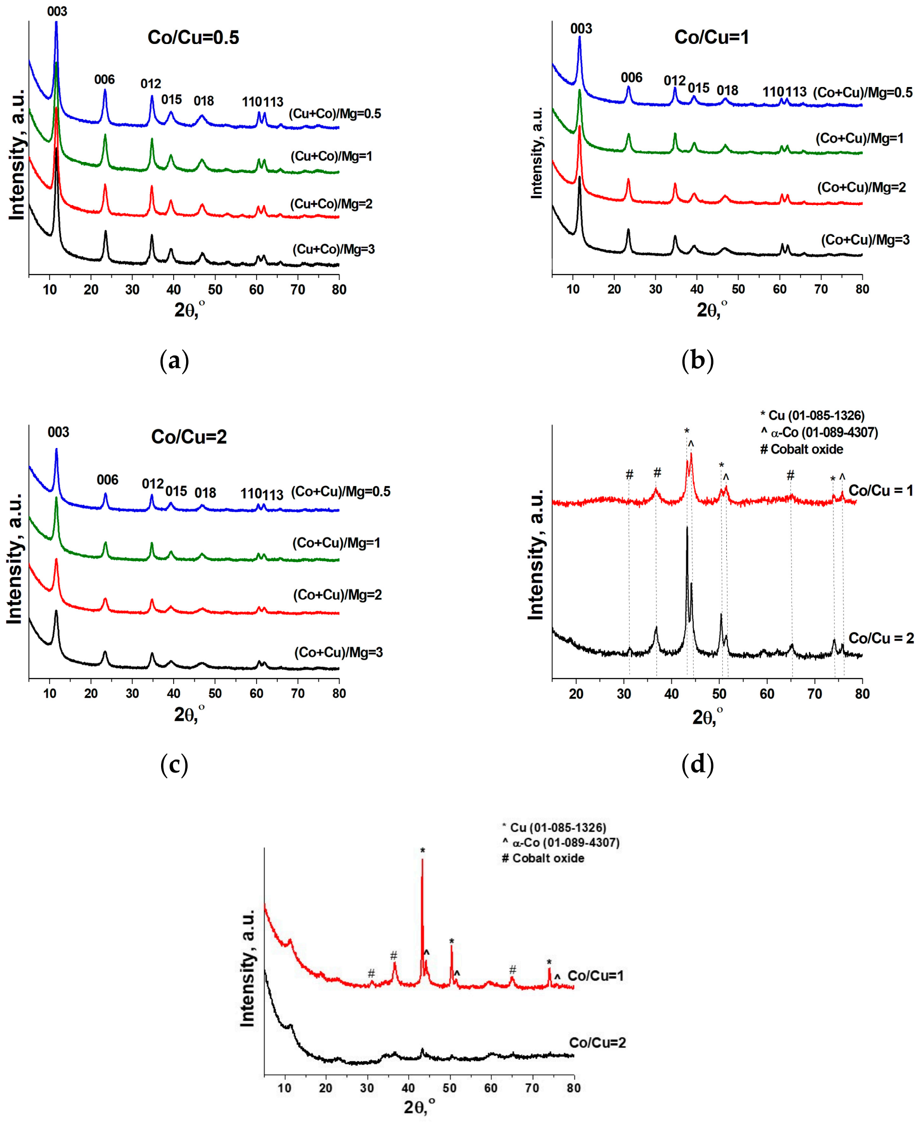
$$Y_i = \frac{moles\ of\ product\ obtained}{moles\ of\ initial\ FAL} * 100\% \tag{3}$$

3. Results

3.1. Study of Phase Transformations of the CuCoMgAl-Systems

In this work, the possibility of the preparation of CuCoMgAl-systems in a wide range of metals ratio by coprecipitation was studied. The catalysts' properties largely depend on the phase composition of the corresponding hydroxide phases. Therefore, the important stage of study was the phase composition and structural properties of the CuCoMgAl-hydroxides.

The CuCoMgAl-systems were obtained by changing the ratios of Co/Cu = 0.5, 1, and 2; and (Cu + Co)/Mg = 0.5, 1, 2, and 3. The phase composition of as-synthesized CuCoMgAl-samples was studied by XRD. According to the obtained data (Figure 1a–c), for systems with any ratio of Co/Cu and (Cu + Co)/Mg, the 003 and 006 set of reflections were observed in the low angle areas; the 012, 015, and 018 reflections were observed in the area of medium angles; and the 110 and 113 reflections were observed in the region of high angles. These reflections are characteristic of LDH structures. This indicates the successful production of single-phase layered hydroxides, without the presence of any undesirable side phases.



(**a**) (**b**)

(**c**) (**d**)

(**e**)

Figure 1. XRD patterns of CuCoMgAl-systems: synthesized samples with the ratio (**a**) Co/Cu = 0.5, (**b**) Co/Cu = 1, and (**c**) Co/Cu = 2; (**d**) samples with the ratio Co/Cu = 1 and Co/Cu = 2 at ratio (Co + Cu)/Mg = 2 after calcination and reduction at 800 °C; (**e**) samples with ratio Co/Cu = 1 and Co/Cu = 2 at ratio (Co + Cu)/Mg = 2 after hydrogenation of furfural.

According to the calculated microstructural parameters, the increase of lattice parameter *a* was observed with rise of the (Co + Cu)/Mg ratio in the group with the same

Co/Cu ratio (Table 1). This was due to the introduction of more Co^{2+} (0.650 Å) and Cu^{2+} (0.690 Å) cations with greater ionic radiuses compared with Al^{3+} (0.535 Å) in MgAl-LDH (in accordance with data found in the literature, cell parameter a is equal 3.044 Å for the MgAl-LDH with Mg/Al = 2 [26]). Thus, for the systems with Co/Cu = 0.5, cell parameter a gradually increased from 3.052 to 3.060 Å with the rise of (Co + Cu)/Mg from 0.5 to 3. For the samples with different Co/Cu ratios with the same (Cu + Co)/Mg ratio, the value of parameter a was similar due to almost the same radius of introduced cations. The value of the lattice parameter c remained almost unchanged, which was due to both the constant charge of the layers and the same number of interlayer anions, and the unchangeable ratio of $(Cu^{2+} + Co^{2+} + Mg^{2+})/Al = 2$. The discovered regularities prove that Co and Cu cations were embedded in the structures of layered hydroxides as a result of the synthesis. Consequently, the possibility of obtaining single-phase materials with a hydrotalcite-like structure by making fine adjustments to changes in the Co/Cu and (Cu + Co)/Mg ratios is shown. Crystallite sizes in the a and c directions changed slightly for the synthesized samples. Thus, for the samples with the constant Cu/Cu ratio, L_a was almost the same (Co/Cu = 1) or slightly increased (Co/Cu = 0.5 and 2) with the rise of the (Co + Cu)/Mg ratio. For the samples with Co/Cu = 0.5 and 1, crystallite size L_c was bigger for the higher (Co + Cu)/Mg ratio. The reverse trend was observed for the samples with Co/Cu = 2.

Table 1. Microstructural parameters of the CoCuMgAl systems with different ratio of (Co + Cu)/Mg = 0.5; 1; 2; 3; and Co/Cu = 0.5; 1; 2.

Sample with (Co + Cu)/Mg	c, Å	a, Å	L_c, Å	L_a, Å
Lattice parameters for samples with Co/Cu = 0.5				
0.5	22.88	3.052	95	167
1	22.87	3.055	89	138
2	22.86	3.061	97	138
3	22.72	3.060	109	138
Lattice parameters for samples with Co/Cu = 1				
0.5	22.86	3.052	105	169
1	22.88	3.056	101	181
2	22.79	3.059	88	160
3	22.82	3.062	91	148
Lattice parameters for samples with Co/Cu = 2				
0.5	22.87	3.051	76	142
1	22.80	3.056	84	121
2	22.82	3.058	98	166
3	22.76	3.060	105	181

3.2. Study of Catalytic Properties of $CuCoMgAlO_x$ Systems

The catalytic properties of $CuCoMgAlO_x$ systems were studied in the liquid phase hydrogenation of FAL and 5-HMF after their preliminary calcination at 550 °C and reduction in hydrogen flow. The reduction temperature was 800 °C for all studied samples. It was chosen on the basis of TPR data and provided full reduction of catalytically active metals [27].

According to obtained data, FAL conversion increased with the increase of Co/Cu ratios for the samples with the same (Cu + Co)/Mg ratio (Figure 2). For the samples with Co/Cu = 0.5 FAL, conversion did not exceed 7%. In the group of samples with the same Co/Cu ratio, an extreme dependence of FAL conversion on the (Cu + Co)/Mg ratio was observed. So, at Co/Cu = 1, the maximum FAL conversion was equal to 32% for the sample with (Cu + Co)/Mg = 2. The further increase in the proportion of divalent metals in the sample with (Cu + Co)/Mg = 3 led to the decrease of FAL conversion by up to 16%. For the samples with Co/Cu = 2, the FAL conversion reached 40% and 37% for the catalysts with (Cu + Co)/Mg = 1 and 2, respectively (Figure 2).

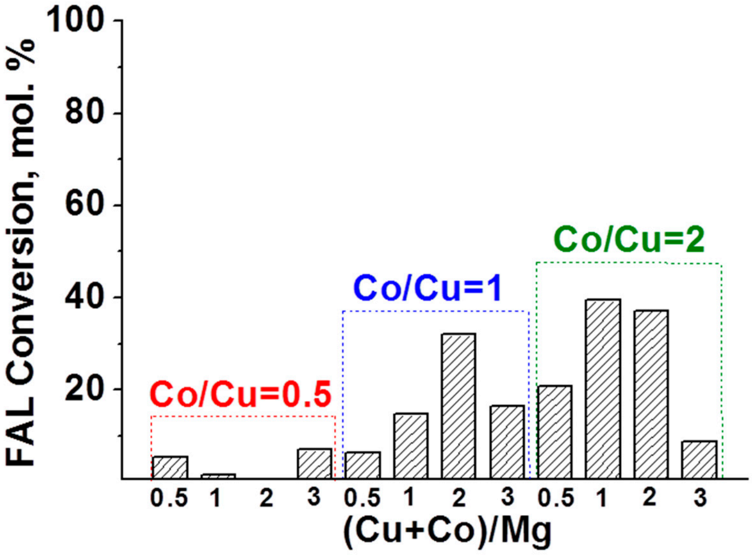


Figure 2. Catalytic activity of $CuCoMgAlO_x$-systems in the FAL hydrogenation (solvent—water).

The unique feature for all studied catalysts was an exceptionally high FOL selectivity (more than 99%), irrespective of both the Co/Cu catalytically active metals, and the portion of Mg in their compositions.

The samples with high Co/Cu molar ratios (Co/Cu = 1 and 2) with (Cu + Co)/Mg = 2 had the best catalytic characteristics in aqua phase FAL hydrogenation. Therefore, the FAL hydrogenation with ethanol (C_2H_5OH) as a solvent was made for these samples, for a more detailed study of the catalytic properties of the $CuCoMgAlO_x$ systems and synergetic effects during the interaction of Cu and Co. It is known that solvent nature has a great impact on catalyst activity, reaction way, and the composition of obtained products [7].

According to obtained data, a significant change in activity was observed when changing the Co/Cu ratio with the use of ethanol as a solvent (Figure 3). FAL conversion for the sample with Co/Cu = 1 increased from 32 to 42% when replacing water with alcohol. At the same time, a great decrease of the FAL conversion from 37 to 10% was observed with an increase in the Co/Cu ratio of up to 2. It is known that there are two main functions of the solvent in the reaction. The first one is the interaction with organic substrates, and the second one is the interaction with the surface of metallic catalysts with a change in their reactive ability. The solvent is capable of facilitating desorption of hydrogenation products from the surface of the catalyst by forming hydrogen bonds with them. These aspects are of great interest to researchers, and are valuable methods to control selectivity, if necessary, to minimize by-products [7,28,29]. It is important to note that the change in the solvent did not affect the direction of FAL transformations. FOL was the main product, with the selectivity >99%.

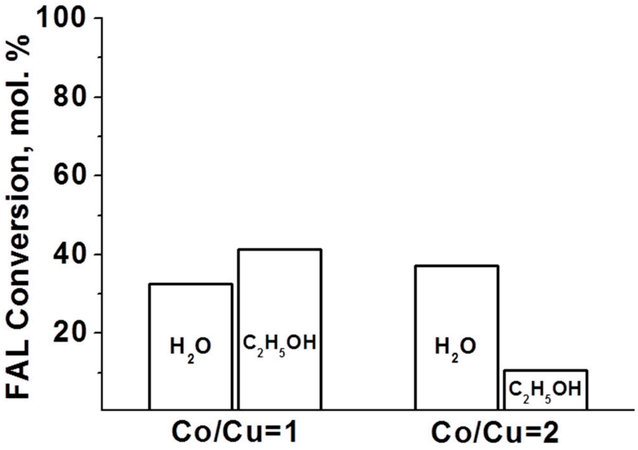


Figure 3. Catalytic activity of samples with ratio Co/Cu = 1 and 2 at ratio (Co + Cu)/Mg = 2 in the FAL hydrogenation (solvent—ethanol).

The catalytic properties of $CuCoMgAlO_x$ systems with Co/Cu = 1 and 2 and (Cu + Co)/Mg = 2 (they had the best catalytic activity in FAL hydrogenation) were studied in the aqua phase hydrogenation of 5-HMF (Table 2). The high 5-HMF conversion achieved 70% and with selectivity to DHMF, more than 90% was discovered for these systems (Table 2).

Table 2. Results of 5-HMF hydrogenation in the presence of catalysts with ratio Co/Cu = 1 and 2 at (Co + Cu)/Mg = 2 in the water *.

Sample **	5-HMF Conversion, %	Selectivity to DHMF, %	Yield of DHMF, %
Co/Cu = 1	73	95	69
Co/Cu = 2	74	90	67

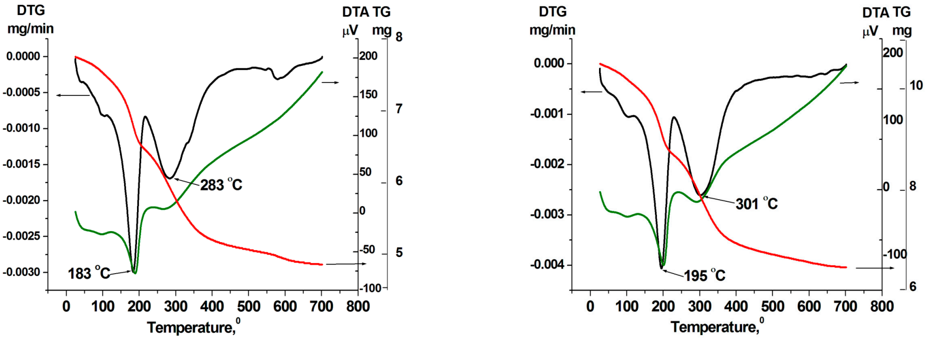
* Temperature—90 °C. Solvent—water. Reaction time—5 h. 5-HMF—5-hydroxymethylfurfural. DHMP—2,5-dihydroxymethylfurfural. ** Ratio (Co + Cu)/Mg = 2.

Therefore, it was shown that the systems based on CuCoMgAl-hydrotalcite-like compounds have extraordinary selectivity with respect to the hydrogenation of C = O groups in the FAL and 5-HMF molecules. At the same time, it is possible to regulate their activity by the change of Co/Cu and (Co + Cu)/Mg. The important characteristics of catalysts are thermal stability and the stability of operation under reaction conditions, in addition to the activity and selectivity of product formation [30]. Thus, it is important to study not only the catalytic properties of the $CuCoMgAlO_x$ systems, but the changes in their phase composition and microstructure. The stability of the catalysts will directly depend on these parameters in the conditions of aqua-phase hydrogenation.

3.3. Study of the Processes Occurred during Formation of Active form of the $CuCoMgAlO_x$ Catalyst

For the creation of an active form of hydrogenation catalyst based on CuCoMgAl-LDH as-synthesized hydrotalcite-like compounds, the materials were preliminary calcined for the preparation of the mixed oxides. Next, the reduction of hydrogenating metals in the hydrogen flow at elevated temperature was performed. It is important to understand how the oxides phase is formed, how the reduction of active metal occurred, what microstructure of the final catalyst is formed, and what changes occur after the reaction. This makes it easier to understand the processes that occur at different stages of catalyst preparation, and probably help to explain observed catalytic properties. For this purpose, the catalysts with the best catalytic properties in the FAL and 5-HMF hydrogenation (Co/Cu = 1 and 2, (Cu + Co)/Mg = 2) reactions were chosen.

The processes occurring during the oxide phase formation were studied using thermal analysis (Figure 4). Two areas of mass loss were observed for these systems: the first was in the temperature range of 130–220 °C, with a maxima of mass loss at 183 and 195 °C, and the second was in the range of 240–450 °C, with a maxima of temperature of 283 and 301 °C, for samples with a ratio of Co/Cu = 1 and 2, respectively. According to data from the literature, the removal of adsorbed water occurs in the first stage of mass loss, and the dehydroxylation of brucite-like layers and the removal of interlayer anions take place at higher temperatures for the samples with LDH structures [31]. The weight loss at the first stage was 13.1–13.4%, and at the second stage was 17.5–18.3% for the samples with Co/Cu = 1 and 2, respectively. Such thermal behavior of synthesized systems serves as additional proof of the formation of a single-phase LDH structure.



(**a**) (**b**)

Figure 4. Curves of TG (red lines), DTG (black lines), and DTA (green lines) for samples with ratio: (**a**)—Co/Cu = 1; and (**b**)—Co/Cu = 2 at ratio (Co + Cu)/Mg = 2.

The shift of the maximum temperature of weight loss to the higher temperature range was observed with an increasing of cobalt content in the hydroxide composition. This indicates an increase in the decomposition temperature of the layered structure of this sample, even with such a slight change in composition.

It is known that reduced metal particles are the active sites of metallic catalysts for hydrogenation reactions. Adsorption of the substrate and hydrogen molecules occurs on them [29]. The formation of unique nanoparticles is possible for the bimetallic catalysts. The character of reduction and the temperature maxima of reduction for these particles may be different from monometallic systems. Accordingly, the interaction of each metal component, both among themselves and with the support, has a significant impact on its recoverability.

In accordance with TPR data, the reduction process of $CuCoMgAlO_x$-mixed oxides occurred stepwise. The first stage of metal reduction was observed in the temperature range of 150–200 °C. It was characterized by a narrow, high-intensity peak, with maximum hydrogen consumption occurring at 171 °C and 173 °C for the samples with Co/Cu = 1 and 2, respectively (Figure 5). At the second stage, a wide, low-intensity area of hydrogen consumption was observed at higher temperatures (350–700 °C). Such stepwise reduction characteristics may be explained by the presence of both monometallic oxides, CuO and Co_3O_4, and mixed oxides, $CuAlO_x$, $CoAlO_x$, and non-stoichiometric $CuCoAlO_x$, in the composition of the $CuCoMgAlO_x$-mixed oxides after their calcination.

According to our previously obtained data, the copper reduction from $CuAlO_x$ mixed oxide obtained from LDH occurred in a single stage and was characterized by the reduction of the maximum temperature in the range of 200 to 300 °C, in accordance with the equation:

$$CuO + H_2 \rightarrow Cu^0 + H_2O \quad (4)$$

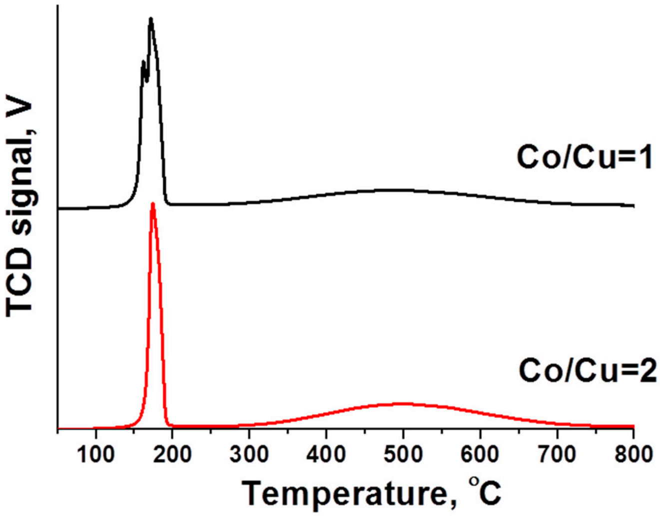


Figure 5. TPR profiles of samples with ratio Co/Cu = 1 and 2 at ratio (Co + Cu)/Mg = 2.

The reduction of cobalt from $CoAlO_x$ obtained from LDH occurred in two stages. It consisted of the reduction of Co_3O_4 to CoO with a maximum temperature of 380 °C, and a further reduction of CoO to metallic Co in the range 600–750 °C, with maximum at 673 °C [27,32]. The extended high-temperature reduction region of 300–750 °C may be associated with the presence of highly dispersed metal particles strongly bound to the surface of the support and coarse hard-to-reduce particles. An increase in the Co/Cu ratio contributed to a slight shift in the maximum reduction temperature of metals from the corresponding oxides to a higher temperature region. It is important to note that for the $CuCoMgAlO_x$-mixed oxides with magnesium cations in the composition, the reduction of metals was observed at lower temperatures compared to $CuAlO_x$ and $CoAlO_x$ [33].

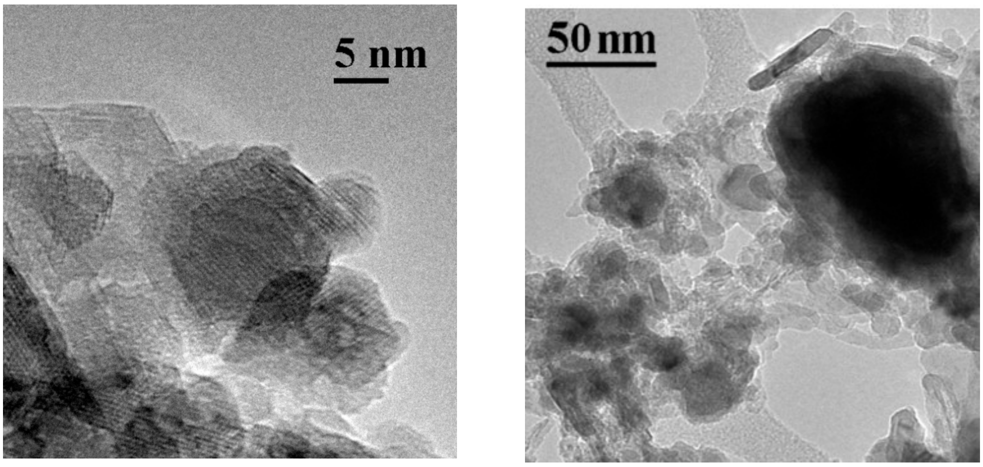
The total amount of hydrogen consumed during the reduction process enhanced with the rise of Co/Cu. For the sample with Co/Cu = 1, the amount of consumed hydrogen was 7.75 mmol/g, and for the sample with Co/Cu = 2, this parameter was 8.35 mmol/g (the (Cu + Co)/Mg was constant and equal 2) (Table 3). Therefore, it is probable that some part of the metals remained unreduced for the sample with Co/Cu = 2. According to XRD data, the phase composition of the samples after calcination and reduction, represented by the mixture of metallic α-Co (ICDD PDF-2 01-089-4307, face-centered cubic, Fm-3m), Cu (ICDD PDF-2 01-085-1326, face-centered cubic, Fm-3m), and the mixed oxide phase, came close to the structure of Co_3O_4 (ICDD PDF-2 00-042-1467, face-centered cubic, Fd-3m,) irrespective of Co/Cu ratio (Figure 1d). It is most likely that the composition of the presented oxide phase also included Al cations, which always occur in systems obtained after high-temperature treatments of hydrotalcite-like phases [27,33,34]. It is not possible to estimate the proportion of unreduced Co and Cu included in the mixed-oxide phase.

Table 3. TPR data for CuCoMgAlOx—systems with ratio Co/Cu = 1 and 2 at ratio (Co + Cu)/Mg = 2.

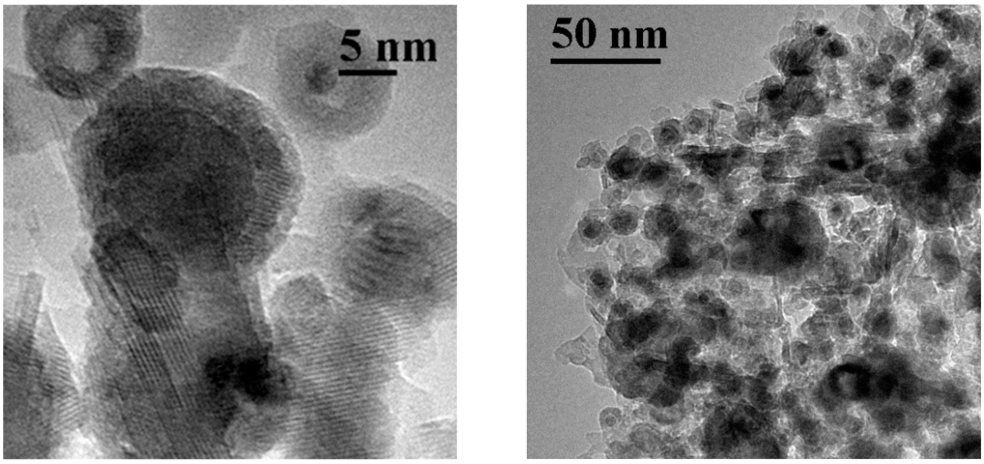
Sample *	T_{Max}, °C	n_{H2}, mmol/g
Co/Cu = 1	171 ~480	4.62 3.13
Co/Cu = 2	174 ~500	3.88 4.47

* Ratio (Co + Cu)/Mg = 2.

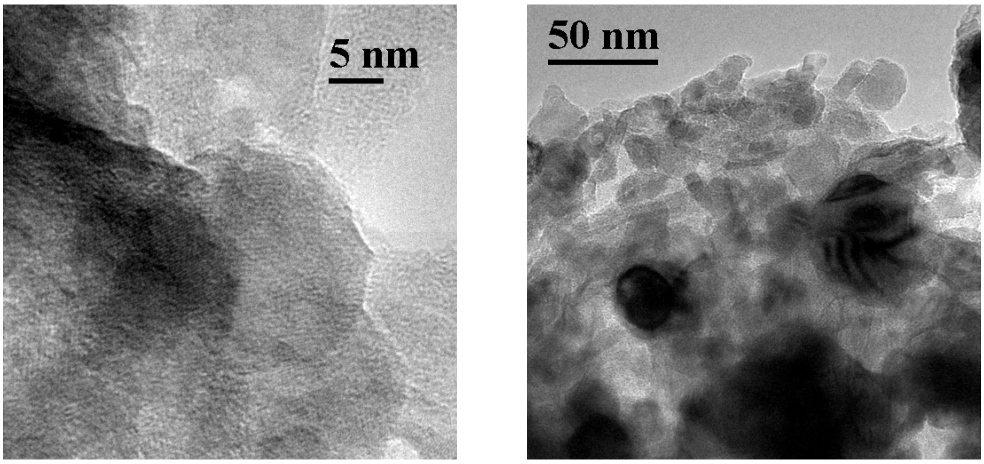
Often, changes in the microstructures of catalysts, the particle sizes of active metals, metals sintering, etc., was observed during the reaction. Ultimately, this can have a significant impact on the stability of the samples. It is very important since, as noted earlier, one of the disadvantages of Co and Cu-containing FAL hydrogenation catalysts is their rapid deactivation [7]. Therefore, the samples with Co/Cu = 1 and (Co + Cu)/Al = 2 both after calcination and reduction, and after the reaction of the aqua phase FAL hydrogenation were studied by TEM (Figure 6).



(**a**) Co/Cu = 1 − R

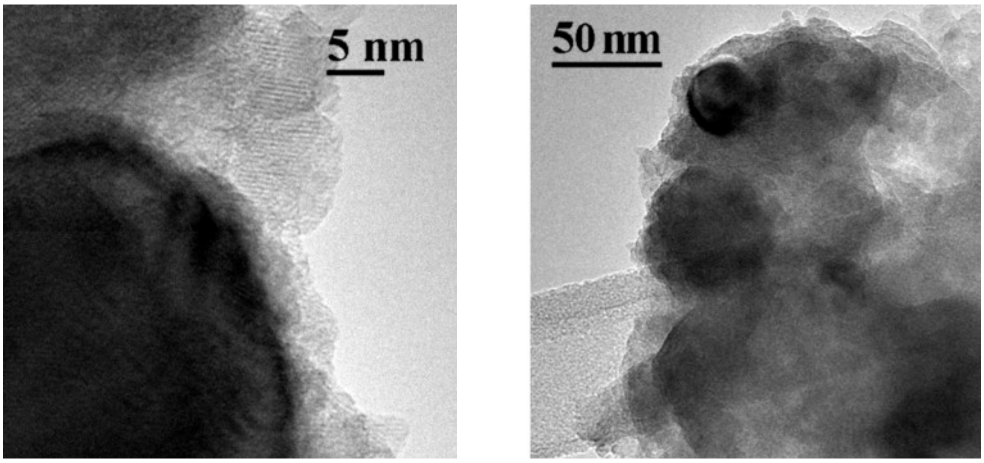


(**b**) Co/Cu = 2 − R



(**c**) Co/Cu = 1 − F

Figure 6. *Cont.*



(**d**) Co/Cu = 2 – F

Figure 6. Micrographs of samples with the ratio Co/Cu = 1 and 2 at ratio (Co + Cu)/Mg = 2 before the reaction (**a**) Co/Cu = 1 − R and (**b**) Co/Cu = 2 − R and after the reaction (**c**) Co/Cu = 1 − F and (**d**) Co/Cu = 2 − F.

According to TEM data, the surfaces of studied samples after the calcination and reduction steps (before reaction) had a «core-shell» structure, regardless of Co/Cu ratio (Figure 6a,c). The metallic Cu and Co particles were in the «core». The average metallic particle size was 12. 7 nm. «Shell» consisted of non-stoichiometric $CuCoMgAlO_x$ mixed oxides. The obtained TEM results are consistent with the XRD data for these samples (Figure 1d).

The processes occurring during the reaction of the aqua phase hydrogenation of FAL had a greater effect on the phase composition of the samples than on their microstructural characteristics. The changes were dependent on the Co/Cu ratio in the catalyst's composition. According to XRD data, the phase composition of the sample with Co/Cu = 1 − F (Co/Cu = 1) was unchangeable after the reaction (Figure 1e). Clear reflections corresponding to the metallic Co, Cu phases and the mixed oxide phase with a structure close to Co_3O_4 are presented in the diffractograms. The sample with a higher Co/Cu ratio (Co/Cu = 2 − F) was X-ray amorphous after the reaction (Figure 1e). Consequently, its structural stability was lower compared to the sample with Co/Cu = 1. In the future, this may significantly affect the stability of the catalyst. In accordance with TEM data, there was no sintering or change in the size of metallic particles after the reaction for the studied samples. This is a positive result and confirms the prospects of studying bimetallic CuCo-systems for the hydrogenation reaction of furan compounds (FAL and 5-HMF). At the same time, carbon deposits formed on the surface of the catalysts after the reaction for both samples (Figure 6c,d). This provides a basis for the further research and improvement of these systems. In addition to the microstructure, the properties of catalysts can be greatly influenced by the surface ratio of hydrogenating metals and their electronic state. Therefore, in subsequent works we plan to study the catalysts based on CuCoMgAl-layered hydroxides before and after the reaction by the XPS method.

Thus, it was demonstrated that the catalyst samples prepared with identical hydrotalcite-type structures had different catalytic properties depending on the Co/Cu molar ratios. At the same time, the catalysts with close catalytic properties but different Co/Cu ratios had different thermal stabilities, hydrogenation metals reductions, and microstructures. In the future, this may significantly affect the stability of these catalysts in more severe catalytic conditions or during resource tests.

4. Conclusions

1. In this study, CuCoMgAl-systems with LDH structure in a wide range of ratios (Co + Cu)/Mg = 0.5, 1, 2, and 3; and Co/Cu = 0.5, 1, and 2 were successfully prepared.

The possibility of fine-tuning the properties of the samples by changing the ratios is shown.

2. The value of the Co/Cu ratio has a significant impact on the formation of the oxide phase and the metal reduction process. An increase in the Co/Cu ratio in the composition of the systems contributed to the shift of the maxima of the decomposition temperatures of hydroxides and the reduction of metals (Cu, Co) to a higher temperature region, and, accordingly, an increase in thermal stability.
3. Catalysts based on CuCoMgAl-layered hydroxides showed a high selectivity of carbonyl group hydrogenation in FAL and 5-HMF. The FOL selectivity for all studied systems was more than 99%, irrespective of their composition and the solvent used. The selectivity for DHMF was 95% on 5-HMF hydrogenation.
4. The surfaces of the samples with different Co/Cu ratios (Co/Cu = 1 and 2) after calcination and reduction was the same and had a «core-shell» structure. «Core» consisted of copper and cobalt metallic particles with an average size of 12.7 nm. «Shell» consisted of $CuCoMgAlO_x$ non-stoichiometric spinel oxides. In the aqua phase FAL hydrogenation condition, the composition of the catalysts varied to a greater extent than their microstructures. The change in the phase composition also depended on the value of Co/Cu ratios. For the sample with Co/Cu = 1, the phase composition remained unchanged after the reaction. The decrease in the structural stability of the samples with the increase in Co/Cu ratios was observed (according to XRD data, the sample with Co/Cu = 2 was X-ray amorphous). The differences in the properties of the active phase, which is formed at the stage of high-temperature treatments, means that even a small change in the ratios (Co/Cu = 1 and 2) contributed to a change in thermal stability, completeness, and the ease of the reduction of metals, as well as to different phase composition after the reaction.

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References

1. Chien Truong, C.; Kumar Mishra, D.; Hyeok Ko, S.; Jin Kim, Y.; Suh, Y.W. Sustainable Catalytic Transformation of Biomass-Derived 5-Hydroxymethylfurfural to 2, 5-Bis (hydroxymethyl) tetrahydrofuran. *ChemSusChem* **2022**, *15*, e202200178. [CrossRef] [PubMed]
2. Srivastava, S.; Jadeja, G.C.; Parikh, J. A versatile bi-metallic copper–cobalt catalyst for liquid phase hydrogenation of furfural to 2-methylfuran. *RSC Adv.* **2016**, *6*, 1649–1658. [CrossRef]
3. Wang, Y.; Wang, H.; Kong, X.; Zhu, Y. Catalytic Conversion of 5-Hydroxymethylfurfural to High-Value Derivatives by Selective Activation of C−O, C=O, and C=C Bonds. *ChemSusChem* **2022**, *15*, e202200421. [CrossRef]
4. Xu, W.; Xia, Q.; Zhang, Y.; Guo, Y.; Wang, Y.; Lu, G. Effective production of octane from biomass derivatives under mild conditions. *ChemSusChem* **2011**, *4*, 1758–1761. [CrossRef]
5. Román-Leshkov, Y.; Barrett, C.J.; Liu, Z.Y.; Dumesic, J.A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447*, 982–985. [CrossRef]
6. Kazi, F.K.; Patel, A.D.; Serrano-Ruiz, J.C.; Dumesic, J.A.; Anex, R.P. Techno-economic analysis of dimethylfuran (DMF) and hydroxymethylfurfural (HMF) production from pure fructose in catalytic processes. *Chem. Eng. J.* **2011**, *169*, 329–338. [CrossRef]

7. Singh, G.; Singh, L.; Gahtori, J.; Gupta, R.K.; Samanta, C.; Bal, R.; Bordoloi, A. Catalytic hydrogenation of furfural to furfuryl alcohol over chromium-free catalyst: Enhanced selectivity in the presence of solvent. *Mol. Catal.* **2021**, *500*, 111339. [CrossRef]
8. Manikandan, M.; Venugopal, A.K.; Nagpure, A.S.; Chilukuri, S.; Raja, T. Promotional effect of Fe on the performance of supported Cu catalyst for ambient pressure hydrogenation of furfural. *RSC Adv.* **2016**, *6*, 3888–3898. [CrossRef]
9. Yuan, Q.; Zhang, D.; van Haandel, L.; Ye, F.; Xue, T.; Hensen, E.J.; Guan, Y. Selective liquid phase hydrogenation of furfural to furfuryl alcohol by Ru/Zr-MOFs. *J. Mol. Catal. A–Chem.* **2015**, *406*, 58–64. [CrossRef]
10. Feng, L.; Li, X.; Lin, Y.; Liang, Y.; Chen, Y.; Zhou, W. Catalytic hydrogenation of 5-hydroxymethylfurfural to 2, 5-dimethylfuran over Ru based catalyst: Effects of process parameters on conversion and products selectivity. *Renew. Energy* **2020**, *160*, 261–268. [CrossRef]
11. Silva, W.R.; Matsubara, E.Y.; Rosolen, J.M.; Donate, P.M.; Gunnella, R. Pd catalysts supported on different hydrophilic or hydrophobic carbonaceous substrate for furfural and 5-(hydroxymethyl)-furfural hydrogenation in water. *Mol. Catal.* **2021**, *504*, 111496. [CrossRef]
12. Byun, M.Y.; Park, D.W.; Lee, M.S. Effect of oxide supports on the activity of Pd based catalysts for furfural hydrogenation. *Catalysts* **2020**, *10*, 837. [CrossRef]
13. Mironenko, R.M.; Talsi, V.P.; Gulyaeva, T.I.; Trenikhin, M.V.; Belskaya, O.B. Aqueous-phase hydrogenation of furfural over supported palladium catalysts: Effect of the support on the reaction routes. *React. Kinet. Mech. Catal.* **2019**, *126*, 811–827. [CrossRef]
14. Merlo, A.B.; Vetere, V.; Ruggera, J.F.; Casella, M.L. Bimetallic PtSn catalyst for the selective hydrogenation of furfural to furfuryl alcohol in liquid-phase. *Catal. Commun.* **2009**, *10*, 1665–1669. [CrossRef]
15. Redina, E.A.; Vikanova, K.V.; Kapustin, G.I. Monometallic Copper Catalysts for the Hydrogenation of 5-Hydroxymethylfurfural. *Russ. J. Phys. Chem. A* **2020**, *94*, 2558–2562. [CrossRef]
16. Endot, N.A.; Junid, R.; Jamil MS, S. Insight into biomass upgrade: A review on hydrogenation of 5-Hydroxymethylfurfural (HMF) to 2, 5-Dimethylfuran (DMF). *Molecules* **2021**, *26*, 6848. [CrossRef]
17. Jiang, Z.; Zeng, Y.; Hu, D.; Guo, R.; Yan, K.; Luque, R. Chemical transformations of 5-hydroxymethylfurfural to highly added value products: Present and future. *Green Chem.* **2023**, *25*, 871–892. [CrossRef]
18. Yang, P.; Cui, Q.; Zu, Y.; Liu, X.; Lu, G.; Wang, Y. Catalytic production of 2, 5-dimethylfuran from 5-hydroxymethylfurfural over Ni/Co_3O_4 catalyst. *Catal. Commun.* **2015**, *66*, 55–59. [CrossRef]
19. Nguyen-Huy, C.; Lee, H.; Lee, J.; Kwak, J.H.; An, K. Mesoporous mixed CuCo oxides as robust catalysts for liquid-phase furfural hydrogenation. *Appl. Catal. A–Gen.* **2019**, *571*, 118–126. [CrossRef]
20. Chen, B.; Li, F.; Huang, Z.; Yuan, G. Carbon-coated Cu-Co bimetallic nanoparticles as selective and recyclable catalysts for production of biofuel 2, 5-dimethylfuran. *Appl. Catal. B–Environ.* **2017**, *200*, 192–199. [CrossRef]
21. Mascolo, G.; Mascolo, M.C. On the synthesis of layered double hydroxides (LDHs) by reconstruction method based on the "memory effect". *Microporous Mesoporous Mater.* **2015**, *214*, 246–248. [CrossRef]
22. Sun, K.; Liu, Z.; Song, S.; Liu, W.; Wang, P.; Zhang, T.; Xue, Y.; Wang, Y.; Tan, Y. Effect of hydroxyl groups on CuCoMg nanosheets for ethanol and higher alcohol synthesis from syngas. *Ind. Eng. Chem. Res.* **2021**, *60*, 2388–2399. [CrossRef]
23. Stepanova, L.N.; Belskaya, O.B.; Vasilevich, A.V.; Leont'eva, N.N.; Baklanova, O.N.; Likholobov, V.A. Effect of the composition of initial components and the conditions of activation on the mechanochemical synthesis of magnesium–aluminum layered double hydroxides. *Kinet. Catal.* **2018**, *59*, 521–531. [CrossRef]
24. Lee, S.B.; Ko, E.H.; Park, J.Y.; Oh, J.M. Mixed metal oxide by calcination of layered double hydroxide: Parameters affecting specific surface area. *Nanomaterials* **2021**, *11*, 1153. [CrossRef]
25. Bukhtiyarova, M.V. A review on effect of synthesis conditions on the formation of layered double hydroxides. *J. Solid State Chem.* **2018**, *269*, 494–506. [CrossRef]
26. Stepanova, L.N.; Belskaya, O.B.; Likholobov, V.A. Effect of the nature of the active-component precursor on the properties of Pt/$MgAlO_x$ catalysts in propane and n-decane dehydrogenation. *Kinet. Catal.* **2017**, *58*, 383–391. [CrossRef]
27. Stepanova, L.N.; Mironenko, R.M.; Kobzar, E.O.; Leont'eva, N.N.; Gulyaeva, T.I.; Vasilevich, A.V.; Serkova, A.N.; Salanov, A.N.; Lavrenov, A.V. Synthesis of CuAl-, CoAl-, and CuCoAl-Catalysts from Layered Hydroxides for Furfural Hydrogenation. *Eng* **2022**, *3*, 400–411. [CrossRef]
28. Taylor, M.J.; Durndell, L.J.; Isaacs, M.A.; Parlett, C.M.; Wilson, K.; Lee, A.F.; Kyriakou, G. Highly selective hydrogenation of furfural over supported Pt nanoparticles under mild conditions. *Appl. Catal. B–Environ.* **2016**, *180*, 580–585. [CrossRef]
29. Singh, U.K.; Vannice, M.A. Kinetics of liquid-phase hydrogenation reactions over supported metal catalysts—A review. *Appl. Catal. A–Gen.* **2001**, *213*, 1–24. [CrossRef]
30. Wang, Q.; Feng, J.; Zheng, L.; Wang, B.; Bi, R.; He, Y.; Liu, H.; Li, D. Interfacial structure-determined reaction pathway and selectivity for 5-(hydroxymethyl) furfural hydrogenation over Cu-based catalysts. *ACS Catal.* **2019**, *10*, 1353–1365. [CrossRef]
31. Tan, X.Y.; Ungur, L.; Chin, W.S. Carbonate-free CoAl layered double hydroxides supercapacitors: Controlled precipitation via acid mediated decomplexation. *Appl. Clay Sci.* **2022**, *224*, 106519. [CrossRef]
32. Kobzar, E.O.; Stepanova, L.N.; Leont'eva, N.N.; Gulyaeva, T.I.; Trenikhin, M.V.; Lavrenov, A.V. Effect of the composition and synthesis procedure of catalysts based on CoAl hydroxides on their properties in furfural hydrogenation. *Kinet. Catal.* **2023**, *64*, 473–483. [CrossRef]

33. Arnoldy, P.; Moulijn, J.A. Temperature-programmed reduction of $CoOAl_2O_3$ catalysts. *J. Catal.* **1985**, *93*, 38–54. [CrossRef]
34. Ribet, S.; Tichit, D.; Coq, B.; Ducourant, B.; Morato, F. Synthesis and activation of Co–Mg–Al layered double hydroxides. *J. Solid State Chem.* **1999**, *142*, 382–392. [CrossRef]