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Review

# Mixed-Oxide Catalysts with Spinel Structure for the Valorization of Biomass: The Chemical-Loop Reforming of Bioethanol

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**Abstract:** This short review reports on spinel-type mixed oxides as catalysts for the transformation of biomass-derived building blocks into chemicals and fuel additives. After an overview of the various methods reported in the literature for the synthesis of mixed oxides with spinel structure, the use of this class of materials for the chemical-loop reforming of bioalcohols is reviewed in detail. This reaction is aimed at the production of H<sub>2</sub> with intrinsic separation of C-containing products, but also is a very versatile tool for investigating the solid-state chemistry of spinels.

**Keywords:** spinels; metal ferrites; bioethanol; chemical-loop reforming; syngas

## 1. Introduction

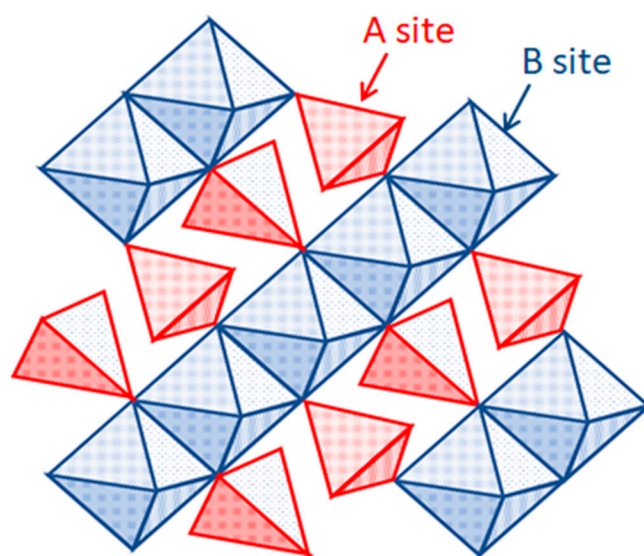
Spinel oxides with the general formula AB<sub>2</sub>O<sub>4</sub> are chemically and thermally stable materials suitable for several applications, including catalysis.

The ideal stoichiometric spinel structure is assumed by oxides with average cation charge of 2.33, like, for instance, magnetite Fe<sub>3</sub>O<sub>4</sub>, with one divalent and two trivalent Fe cations. The presence of cations with different charges is at the basis of most catalytic properties of spinels, allowing internal redox reactions which make easier reduction–reoxidation cycles of the catalyst. In the spinel structure, the oxygen anions are distributed in an approximate cubic close-packing and the cations are distributed in the interstices between the oxygen anions. Only a fraction of the interstices are occupied by cations, namely eight tetrahedral interstices (A sites) and 16 octahedral interstices (B sites) in a cell containing 32 oxygen anions, each anion being located at the corner between two octahedra and one tetrahedron. The occupied cation sites form rows of octahedra joined edge-to-edge and connected by tetrahedra (Figure 1).

The distribution of different cations in the A and B sites essentially depends on their crystal field stabilisation in coordination four or six. The effect of this distribution on catalytic properties is not negligible. When the spinel structure is interrupted by a surface, octahedral B sites are more exposed than tetrahedral A sites. As a consequence, B sites have been considered to represent the most effective catalytic sites [1]. However, this assumption has somehow to be qualified, as the internal charge transfers needed to close a catalytic cycle imply both site B and site A, and both sites are involved in oxygen mobility. Moreover, the reduction of the surface implies a severe reorganisation which

significantly modifies the distribution of the sites [2]. Reduction of the oxide can reach complete destruction of the spinel phase when the material is used as oxygen carrier in a chemical-loop cycle.

The spinel structure is tolerant of significant deviations from the average cation valence 2.33, with significant effects on catalytic activity. The incorporation of cations with higher positive charge is possible if accompanied by the formation of cation vacancies, which allow the charge balance of the solid to be kept. A typical example is  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite), a cation-defective spinel. The absence of divalent Fe<sup>2+</sup> cations in maghemite has been suggested to explain the lower effectiveness of maghemite as Fenton catalyst by comparison with the isostructural not-defective magnetite Fe<sub>3</sub>O<sub>4</sub> [3]. On the contrary, partial oxidation of spinels has been reported to create oxygen defects, on which reactive ·OH radicals are easily formed [4].



**Figure 1.** Spinel structure. Cations occupy the centre of tetrahedra (sites A) and octahedra (sites B). Oxygen anions are at the corner between two octahedra and one tetrahedron.

Overall, versatile catalytic properties are dependent on the chemical composition and nature of substituted ions, charges and their distribution among the octahedral (Oh) and tetrahedral (Td) sites, which in turn are affected by the synthesis method used [5–8]. Indeed, many methods have been developed to synthesize spinel oxides, such as, amongst others, solid-state synthesis (mechanical milling/alloying), and wet chemical routes: sol–gel, coprecipitation, reverse micelles, hydrothermal/solvothermal synthesis, electrochemical synthesis, and others (Table 1).

**Table 1.** Methods reported in the literature for spinel synthesis.

Preparation Method	Reference
Coprecipitation	[9–23]
Sol–gel	[24–46]
Hydrothermal	[47–55]
Solvothermal	[56–60]
Microemulsion/Reverse micelles	[61–68]
Template	[66–72]
Mechanical milling	[73–81]
Plasma	[82,83]
Flux growth	[84–86]
Solid phase	[87]
Combustion	[88–90]
Microwave combustion	[91–93]
Microwave hydrothermal	[94–96]
Pechini method	[97–100]

Table 1. Cont.

Preparation Method	Reference
Electrochemical	[101]
Electrospinning	[102]
Thermal treatment	[103,104]
Ultrasonic wave-assisted ball milling	[105]
Spray pyrolysis	[106]
Aerosol	[107]
Forced hydrolysis	[108]
Glycol-thermal	[109]
Refluxing	[110]

The choice of the preparation method is generally driven by the stability of the specific spinel composition targeted and by the requirement of specific textural, chemical or magnetic properties of the final product. Obtaining particles smaller than 10 nm is usually possible by proper tuning of most low-temperature methods. The temperature of post-treatment is the most important factor affecting the size of the spinel particles. The formation of small particles at high temperature is possible by reducing the time spent at the synthesis temperature, for instance in methods of solution combustion or spray pyrolysis. The stability of these small particles in the temperature and redox conditions of the catalytic application is, however, often questionable. The morphology of the spinel particles has been controlled by combination of pH, temperature and flow conditions in several methods.

The preparation methods largely differ by their economics, their energy requirement and their environmental impact. Classical precipitation methods can be hampered by the need of operating in the high-pH field in which all the concerned cations are out of their solubility domain, with consequent rejection of alkaline wastewaters. Methods aimed at a more precise control of particle size by confinement of the precursors, as the emulsion or template methods, imply the use of relatively costly organic additives. This is also the drawback of methods such as the sol-gel, Pechini or alginate methods, in which the homogeneous dispersion of the precursor cations in a matrix favours the formation of spinels with compositions difficult to form by coprecipitation. Some energy-intensive methods, like flux growth, are not intended to form the high-surface-area materials preferred for catalysis but aim for the formation of materials with specific solid-state properties.

Several uses of spinel-type mixed oxides as catalysts for a variety of reactions have been reported; Table 2 summarizes the main ones.

Table 2. Applications of spinel mixed-metal oxides as catalysts.

Reaction	References
Oxidative cleavage of styrene to benzaldehyde with H <sub>2</sub> O <sub>2</sub>	[5,49]
Oxidation of cyclohexane to cyclohexanol/cyclohexanone with O <sub>2</sub> or H <sub>2</sub> O <sub>2</sub>	[6,7]
Hydroxylation of benzene/phenol to phenol/diphenols with H <sub>2</sub> O <sub>2</sub>	[111]
Oxidation of vanillyl to vanillin with air	[112]
Oxidation of benzyl alcohol to benzaldehyde with H <sub>2</sub> O <sub>2</sub>	[113]
Oxidation of monoterpene alkenes with O <sub>2</sub>	[114]
Oxidation of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid (hmf to fdca) with H <sub>2</sub> O <sub>2</sub> or O <sub>2</sub>	[115–117]
Oxidation of aniline to azoxybenzene with H <sub>2</sub> O <sub>2</sub>	[118]
Oxidation of toluene to benzaldehyde with H <sub>2</sub> O <sub>2</sub>	[119]
Oxidation of ethanol to acetaldehyde with O <sub>2</sub>	[120]
Oxidation of veratryl alcohol to veratryl aldehyde with O <sub>2</sub>	[121]
Ketonisation of butanol to heptanone	[122]
Total oxidation of voc with air	[123]
Friedel–crafts acylation	[124]
Knoevenagel condensation	[125]
Reduction of ketones	[126]
Reduction of nitroarenes	[127]
Methylation (alkylation) of phenolics, aniline, pyridine	[128]
Methanol, ethanol reforming (by means of chemical-loop)	[129–137]

It is shown that most applications investigated are for the oxidation of organic substrates, for example, for the synthesis of aldehydes or acids. In the field of biomass valorization, worthy of note are the recent papers on the oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) with  $O_2$ , and catalytic transformation involving bioalcohols, mainly bioethanol. Recently, Jain et al. reported on the use of spinel catalysts with composition  $Li_2CoMn_3O_8$  as efficient catalysts for the selective oxidation of HMF to FDCA with 80% isolated yield in a gram-scale reaction [116]. The nanocrystalline spinel was synthesized by a gel pyrolysis method using urea and citric acid as complexing agent. Prompted by the activities of Co- and Mn-based homogeneous catalyst systems such as  $Co(OAc)_2/Mn(OAc)_2/HBr$  used in HMF oxidation, spinel  $MnCo_2O_4$ -supported Ru nanoparticles were synthesized and applied as heterogeneous nanocatalysts for HMF oxidation by Mishra et al. [117], under base-free conditions. An important role was ascribed to the acidic sites on the spinel surface in affording 99% yield to FDCA.

## 2. Spinel as Catalysts for the Chemical-Loop Reforming (CLR) of Bioethanol

The reforming of bioethanol, and in general of bioalcohols, to syngas, has been the object of several investigations during the latest years. This reaction can be carried out in the chemical-loop mode, that is, by alternating the bioalcohol and steam over an O-carrier [129–137], the so-called chemical-loop reforming (CLR). Amongst the most promising materials, ferrospinels offer the advantage of a wide flexibility of composition, structural stability and tunable redox properties. On the other hand, the choice of ethanol as reducing agent has also several advantages: its renewable origin, availability in large quantities at low cost, together with the possibility to decompose at a relatively lower temperature with formation of a hydrogen-rich mixture. CLR is aimed at the production of “clean  $H_2$ ” with an inherent  $CO_x$  separation. The main principle of the CLR process is that an oxygen-storage material is first reduced by ethanol stream ( $T = 400\text{--}500\text{ }^\circ\text{C}$ ), and then reoxidized by water ( $T = 300\text{--}450\text{ }^\circ\text{C}$ ) to produce hydrogen and to restore the original oxidation state of the looping material (Figure 2).

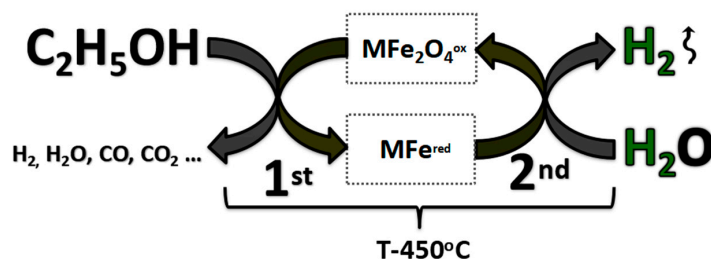


Figure 2. The chemical-loop reforming of ethanol over modified ferrospinels.

Different M-modified  $MFe_2O_4$  spinel-type mixed oxides were synthesized and tested as ionic oxygen and electrons carriers to generate hydrogen by water reduction, after a reductive step of the oxides carried out with ethanol. The aim was to develop materials showing the structural stability needed to undergo complete reversible redox cycling upon chemical looping. Spinel containing Co, Mn, Cu or Cu/Co, Cu/Mn, Co/Mn and alkaline earth metals Ca or Mg as divalent cations were prepared, characterised and tested. The nature of the cations affected the reactivity of the spinels, in regard to both the nature of the products formed during ethanol oxidation along with the purity of the hydrogen produced during the water-reduction step.

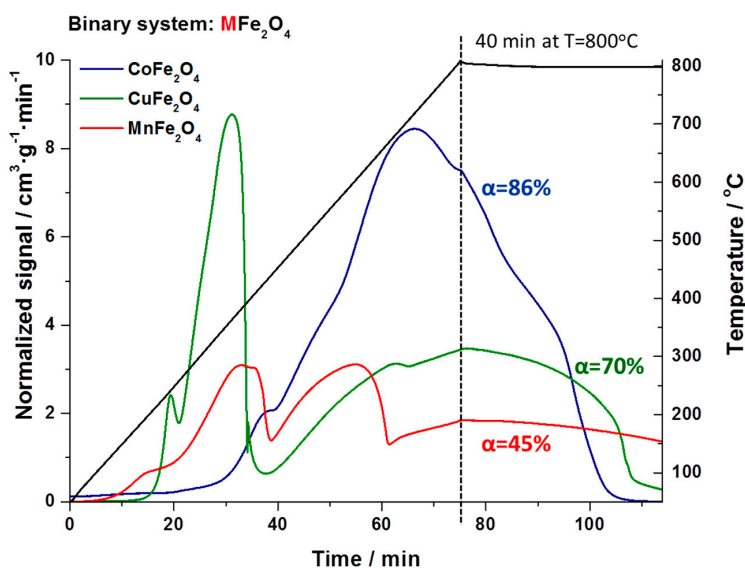
Regarding the behaviour of bare  $Fe_3O_4$ , during the reduction step it formed  $Fe^0$  which then was converted into  $Fe_3C$  (cementite). However, the formed carbide decomposes into metallic iron and carbon ( $Fe_3C \rightarrow 3Fe^0 + C$ ) and in consequence catalyses the growth of graphitic filaments. In order to reduce the formation of coke, a short reduction time of 5 min only was used, since the formation of cementite was slightly delayed at the beginning of the reduction step. The reducibility of magnetite was improved by incorporation of several transition metals like Co, Cu and Ni into the spinel structure.

The structure of  $MFe_2O_4$  ferros spinels, prepared via a coprecipitation route, was identified by means of XRD. A broadening of the diffraction patterns was observed for Mn ferros spinels, that is,  $MnFe_2O_4$ ,  $Cu_{0.5}Mn_{0.5}Fe_2O_4$  and  $Co_{0.5}Mn_{0.5}Fe_2O_4$ , attributed to a decrease in particle size. Table 3 compiles the specific surface area (SSA), the crystallite size (calculated by Scherrer equation) and the particle size of the fresh powders calcined at 450 °C for 8 h.

**Table 3.** Specific surface area (SSA) and crystallite/particle size of spinels with various compositions.

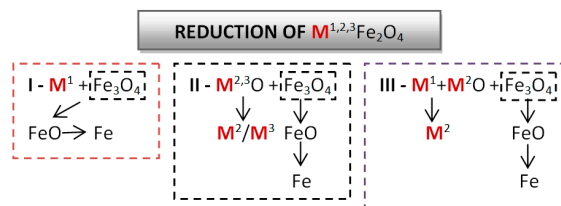
Sample Name	SSA, m <sup>2</sup> /g	Crystallite Size, nm	Particle Size ( $d_{BET}$ ), nm
$CuFe_2O_4$	60	6.9	18.3
$Cu_{0.5}Co_{0.5}Fe_2O_4$	67	10.4	16.5
$CoFe_2O_4$	69	12	16.2
$Co_{0.5}Mn_{0.5}Fe_2O_4$	141	3.5	8
$Cu_{0.5}Mn_{0.5}Fe_2O_4$	112	-	10
$MnFe_2O_4$	165	-	6.9

Temperature-programmed reduction (TPR) was used to characterise the redox properties of samples (Figure 3). The reduction of Fe strongly depends on the presence of another metal in the ferrite. Two main steps of the reduction were shown: (i) the reduction of iron oxide to metallic iron and (ii) the reduction of the incorporated metal oxide to its corresponding metal or sub-oxide. Despite the overlapping of the two steps, based on the nature of the foreign metals and their reduction potentials, combined with the experimental amount of consumed  $H_2$ , it was possible to draw the reduction scheme shown in Figure 4.



**Figure 3.** TPR profile of  $MFe_2O_4$  ferros spinels, where  $M = Cu, Co$  or  $Mn$ ;  $\alpha =$  degree of reduction (%).

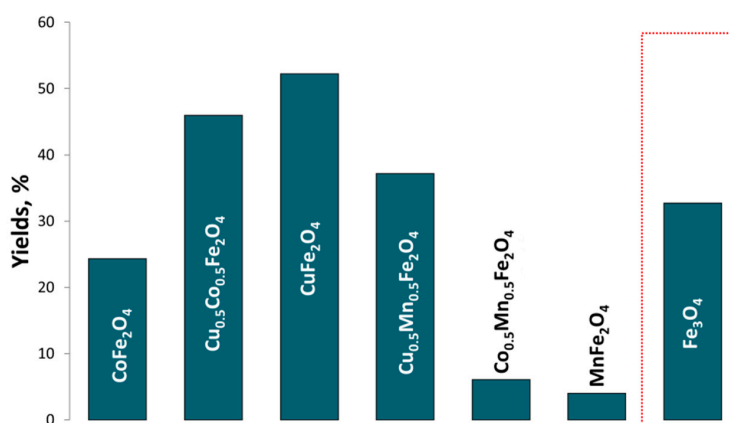
As an example, in the TPR profile of  $CuFe_2O_4$ , a peak at 240 °C can be attributed to the reduction of the copper oxide to the metallic copper, whereas a second peak at ~340 °C can be attributed to a primary stepwise reduction of the spinel with a final formation of  $Cu^0$  and  $Fe_3O_4$ ; the further reduction of  $Fe_3O_4$  to  $FeO$  and of the latter to  $Fe^0$  appears at higher temperatures. In the case of  $CoFe_2O_4$ , primary spinel reduction started to occur at about 400 °C, with a stepwise formation of  $CoO$  and  $Fe_3O_4$ . With the Mn-containing spinel, the reduction of  $MnO$  to metallic Mn turned out to be very difficult, due to its highly negative reduction potential (−1.18 eV), and thus this step occurs only at very high temperatures. In fact, the total reduction extent of  $CoFe_2O_4$  ( $\alpha = 86\%$ ) was much higher than that of  $MnFe_2O_4$  ( $\alpha = 45\%$ ) samples, which can be explained by the formation of the hardly reducible  $MnO$  or of  $Mn_xFe_yO$  oxide.



**Figure 4.** Reduction scheme of  $MFe_2O_4$  ferrospinels.

The reactivity of spinels has been tested in the CLR of bioethanol; the role of the first step, that is, the reduction of the spinel with the alcohol at 450 °C, was aimed at maximizing the spinel reduction extent along with minimizing deactivation, an effect of coke accumulation. In other words, the reduction degree should be monitored as closely as possible, while both limiting the formation of coke, and maintaining the reoxidizability of the material during the second step to regenerate the starting spinel. This condition was essential, in order to allow the looping material to repeat the cycle as many times as possible. Another important point is that during the reduction of the spinel with ethanol, the latter is not only decomposed to light gases (that is, CO, CO<sub>2</sub>, CH<sub>4</sub> and H<sub>2</sub>), but also is oxidised to several compounds, ranging from C2 (acetaldehyde, acetic acid), to C3 (acetone), C4 and higher homologues. These valuable compounds can be easily separated from the light gases and could contribute to the overall process's economic sustainability. The nature and amount of these "by-products" turned out to be a function of spinel composition, as well as of conditions used for the two steps of the chemical loop.

Figure 5 summarizes the integrated values for H<sub>2</sub> produced during the second step, that is, the reoxidation of the reduced  $MFe_2O_4$  spinel (referred to as one complete cycle of 20 min for each one of the two steps) carried out with steam. For a better understanding of the results, some important values are provided in Table 4.



**Figure 5.** Integrated yields for H<sub>2</sub> produced during second reoxidation step carried out with steam at 450 °C and  $MFe_2O_4$  ferrospinels (note: Listed data correspond to the values obtained after 1 complete cycle of 20 min).

The following aspects are worthy of being mentioned:

- Mn incorporation into Fe<sub>3</sub>O<sub>4</sub> with generation of the corresponding ferrites showed its positive aspect on lowering the amount of coke that accumulated during the first step carried out with ethanol, see C %<sub>w</sub> (CHNS) in Table 4;
- Mn incorporation also increased the H<sub>2</sub>/CO<sub>x</sub> ratio, which follows from the previous statement. It is important to notice that the higher the H<sub>2</sub>/CO<sub>x</sub> ratio, the more 'pure' is the H<sub>2</sub> generated

- during the second step. For comparison,  $\text{Fe}_3\text{O}_4$  itself accounts for  $\text{H}_2/\text{CO}_x = 3.5$ , whereas  $\text{MnFe}_2\text{O}_4$  ( $\text{H}_2/\text{CO}_x = 15$ ) and  $\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$  ( $\text{H}_2/\text{CO}_x = 15$ ) showed much higher values;
- (c) the incorporation of Cu (alone, or together with either Co or Mn) has a beneficial effect on the total amount of  $\text{H}_2$  produced from  $\text{H}_2\text{O}$ , compared to  $\text{Fe}_3\text{O}_4$ . Hence, the best performance was shown by  $\text{CuFe}_2\text{O}_4$  (Y-52%),  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  (Y-46%) and  $\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$  (Y-37%);
- (d) incorporation of Cu/Co led to the increase of the  $n_{\text{H}_2}/n_{\text{Eth}}$  ratio, as for  $\text{CuFe}_2\text{O}_4$  ( $n_{\text{H}_2}/n_{\text{Eth}} = 1.2$ ), and  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  ( $n_{\text{H}_2}/n_{\text{Eth}} = 1.0$ ). This can be correlated to the feasibility of producing  $\text{H}_2$  starting from bioethanol being based on the  $\text{H}_2$  vs ethanol heating values (referred to as LHV (Lower Heating Value), MJ/kg): 119, 96 and 28.86, respectively. In other words, the higher the  $n_{\text{H}_2}/n_{\text{Eth}}$ , the higher is the potential efficiency of the CLR process. Of course, there are many more aspects that have to be undertaken in order to calculate the actual cost of the CLR process, and to estimate a final price of  $\text{H}_2$  produced via CLR technology and compare it to the existing ones (not encompassed in this study).

**Table 4.** Chemical-loop process parameters calculated for  $\text{MFe}_2\text{O}_4$  ferrites in bioethanol reforming (note: Listed data correspond to the values obtained after 1 complete cycle of 20 min).

Sample Name	C % <sub>W</sub> after 20 min Red. with Ethanol	$\text{H}_2/\text{CO}_x$	Moles of $\text{H}_2$ /Moles of Ethanol ( $n_{\text{H}_2}/n_{\text{Eth}}$ )
$\text{CoFe}_2\text{O}_4$	11.6	6	0.5
$\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$	16.3	3	1.0
$\text{CuFe}_2\text{O}_4$	6.9	3	1.2
$\text{Cu}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$	6.1	3	0.8
$\text{Co}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$	1.5	15	0.1
$\text{MnFe}_2\text{O}_4$	1.7	15	0.09
$\text{Fe}_3\text{O}_4$	5.3	3.5	0.7

Table 5 summarizes the  $\text{H}_2$  produced during three consecutive cycles of 20 min. The following statements can be made:

- (a) Consecutive utilization of  $\text{CoFe}_2\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4$  and  $\text{Cu}_{0.5}\text{Co}_{0.5}\text{Fe}_2\text{O}_4$  ferros spinels as looping materials resulted in higher amounts of produced hydrogen (given in moles) which surpass the value obtained over the reference material— $\text{Fe}_3\text{O}_4$ ;
- (b) increasing the total *tos* from 20 to 60 min (which accounts the total time for the reduction/reoxidation step) leads to the decreasing of  $\text{H}_2/\text{CO}_x$  ratio, which in its turn affects the final purity of the target gas— $\text{H}_2$ . However, this problem can be overcome by implementation of a three-step CLR process with the third step being carried out with air;
- (c)  $\text{CuFe}_2\text{O}_4$  showed the higher  $n_{\text{H}_2}/n_{\text{Eth}}$  ratio of 1 (referring to the total value for three consecutive cycles) which was in fact twice as high as that obtained with  $\text{Fe}_3\text{O}_4$  ( $n_{\text{H}_2}/n_{\text{Eth}} = 0.5$ );
- (d) on the other hand, under different conditions (not shown here),  $\text{CoFe}_2\text{O}_4$  underwent the greatest extent of reduction during the first step, while being reoxidizable back to the spinel during the second step, and was able to maintain it throughout several repeated cycles. However, it showed the greater amount of accumulated coke, which formed CO when put in contact with steam during the second step;
- (e) coke formation remained an issue for M-modified ferros spinels, which means that avoiding completely carbon deposition and its further accumulation is not possible.



**Table 5.** Chemical-loop process parameters calculated for  $MFe_2O_4$  ferrites in bioethanol reforming (note: Listed data correspond to the values obtained after 3 complete cycles of 20 min).

Sample Name	$H_2/CO_x$	Moles of $H_2$ /Moles of Ethanol
$CoFe_2O_4$	5	0.7
$Cu_{0.5}Co_{0.5}Fe_2O_4$	3	0.9
$CuFe_2O_4$	3	1.0
$Fe_3O_4$	3	0.5

Velasquez Ochoa et al. [138] studied the reduction mechanism of M-modified (Ni, Co and Fe) spinel oxides, where ethanol was the reductant. It was concluded that the first step in ethanol anaerobic decomposition appears to be the same for all samples and corresponds to acetaldehyde formation via dehydrogenation of ethanol. Further reduction of the solid was strongly dependent on the nature of incorporated M (Ni, Co or Fe), viz. acetaldehyde can be either oxidized to acetates ( $NiFe_2O_4$ ), decomposed to CO and  $CH_4$  ( $CoFe_2O_4$ ) or completely oxidized ( $Fe_3O_4$ ). As said above, Mn incorporation significantly reduced the coke formation during the first reduction step, which was attributed to the formation of a thermodynamically stable and hardly reducible layer of  $Mn_xFe_yO$  solid solution. Moreover, it predominantly favored dehydrogenation and condensation reactions leading to the formation of acetaldehyde and acetone, whereas Co/Cu incorporation facilitated total/partial oxidation of ethanol giving rise to high yields of  $H_2$ ,  $CO_x$  and  $H_2O$ .

Recent study on  $CoFe_2O_4$  and  $FeCo_2O_4$  as oxygen carrier materials was performed by Carraro et al. [129,130]. During the reduction step with ethanol,  $FeCo_2O_4$  was reduced faster compared to  $CoFe_2O_4$ . However, its performance during the reoxidation step was quite poor due to an inefficient oxidation by water steam, which is able to oxidize only the outer shell of the nanoparticles, resulting in small  $H_2$  yield. On the other hand,  $CoFe_2O_4$  sample was a more efficient oxygen carrier, which enabled the production of a larger amount of  $H_2$  due to the residual presence of a reducible wüstite, which can be consecutively reoxidized/reduced in further looping cycles.

### 3. Other Materials as O-Carriers for Hydrogen Production via CLR

A comprehensive review on different oxygen carrier materials for the hydrogen production via chemical-loop processes was recently published by Protasova et al. [139]. The review encompasses information on the different perovskites and Ni/Fe/Cu/Ce-based oxygen carrier materials. Perovskites showed good results for the partial oxidation of methane, while with Fe-based materials, promising results also have been obtained. Several research groups have been exploring modifications of simple iron oxide ( $Fe_3O_4$  and  $Fe_2O_3$ ) in order to prevent deactivation [140], to lower the operating temperature [141] and to increase the structural stability and reducibility [142,143], and to increase the reaction rate for oxidation and total efficiency of the process [144]. Several studies were dedicated to different metal additives to iron oxide [145,146]. In addition, ternary metal systems have also been considered in the search for a better synergetic effect [147,148]. Several research groups have investigated the effect of various M-additives on the stability and redox behavior of iron oxide for chemical hydrogen storage using Pd, Pt, Rh, Ru, Al, Ce, Ti, Zr [149] and Al, Cr, Zr, Ga, V, Mo [150]. It was found out that Pd, Pt, Rh and Ru additives have an effect on promoting the reduction and lowering the reoxidation temperature of iron oxide. At the same time, Al, Ce, Ti, Zr, Cr, Ga and V additives prevent deactivation and sintering of iron oxide during repeated redox cycles. Some recent studies on developing of the novel and efficient oxygen carrier materials for chemical-loop applications highlight the special interest in spinel oxides [151–160] which, first of all, were explained by their ability to form thermodynamically stable spinel oxides which allow one to reobtain the initial spinel phase upon cycling, and in turn, increase the stability of the looping material itself.

#### 4. Conclusions

Spinel-type mixed-metal oxides are extremely versatile systems useful as catalysts for a variety of reactions. Because of their chemical–physical properties, they are now studied for redox reactions involving biomass-derived building blocks aimed at the production of either chemicals or fuel components. An example is the reforming of bioalcohols into  $\text{CO}_x/\text{H}_2$ ; this reaction can be carried out in the chemical-loop mode, which in principle should allow the intrinsic separation of  $\text{H}_2$  from  $\text{CO}_x$ . The reaction also allows the study of the chemical–physical properties of spinels in terms of redox properties. Depending on the spinel composition, it is possible to obtain  $\text{H}_2$  along several cycles, but during the spinel reduction step (with the bioalcohol) unfortunately also coke forms, which brings about the formation of  $\text{CO}_x$  during the spinel reoxidation step; the latter, however, should be aimed at the production of  $\text{H}_2$  only. Studies showed that a complete recovery of the initial cycling material was possible, although a slow accumulation of coke takes place (1.0 wt % after 20 cycles or 100 min). This problem could be solved by periodically adding a third step to burn this coke left over by air.

If the production of only  $\text{H}_2$  in the second chemical looping step is not a crippling issue, the process can be envisaged to valorize bioethanol. In fact, quite interestingly, the reduction of the spinel with ethanol also leads to the coproduction of several chemicals, from acetaldehyde to acetone and  $\text{C}_4$  compounds, the relative amount of which is greatly affected by the spinel composition. The valorization of these compounds could help to render economically sustainable the industrial process.

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