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Efficient Catalytic Conversion of Ethanol to 1-Butanol via the Guerbet Reaction over Copper- and Nickel-Doped Porous

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S Supporting Information

ABSTRACT: The direct conversion of ethanol to higher value 1-butanol is a catalytic transformation of great interest in light of the expected wide availability of bioethanol originating from the fermentation of renewable resources. In this contribution we describe several novel compositions of porous metal oxides (PMO) as highly active and selective catalysts for the Guerbet coupling of ethanol to 1-butanol in the temperature range 180–320 °C. The novel PMO catalysts that do not contain any noble metals are obtained by calcination of a series of hydrotalcite precursors synthesized through modular procedures. In particular, catalyst compositions simultaneously containing Cu and Ni dopants have shown excellent catalytic activities. Up to 22% 1-butanol yield at 56% ethanol conversion was reached in a batch mode; recycling and leaching tests showed excellent robustness of the new catalysts. An extensive characterization by means of several techniques such as powder XRD, SEM, TEM, BET, and NH₃- and CO₂-TPD was performed in order to understand structure–activity trends.

KEYWORDS: Bioethanol, 1-Butanol, Guerbet reaction, Copper, Porous metal oxides

INTRODUCTION

Ethanol obtained by fermentation of renewable biomass currently represents one of the largest volume liquid biofuels produced worldwide.^{1,2} Because of the recently established biorefineries capable of processing nonedible lignocellulose feedstocks such as agricultural or forestry waste, its amount is expected to increase by 4–6% annually to 30 billion gallons in the next 5 years.³ The most common application of bioethanol is its use as a blending agent with gasoline; however, a relatively low energy density compared to gasoline (24 MJ/L vs 34.2 MJ/L) and miscibility with water restrict its application in the transportation sector.⁴ As an excellent alternative, 1-butanol possesses an energy density closer to gasoline (29.2 MJ/L), and poor solubility in water (74 g/L at 25 °C).⁵ Moreover, 1-butanol can also be converted to C4-olefins (butenes), which are precursors to other valuable commodity chemicals.⁶ Therefore, the efficient conversion of ethanol to 1-butanol is of great interest for the modern biobased economy. A direct chemical route to 1-butanol relies on the self-coupling of ethanol through the Guerbet reaction.⁷ Innovative homogeneous catalytic methods using Ru^{8–10} and Ir¹¹ complexes have shown excellent selectivity toward 1-butanol under relatively mild reaction conditions.

Heterogeneous catalysts reported for this transformation have been recently summarized in excellent reviews.^{7,12} An overview of selected results in the Guerbet coupling of ethanol to 1-butanol is also summarized in Tables S1 and S2 with the corresponding references.

Frequently used heterogeneous catalysts reported for the Guerbet reaction include MgO,¹³ Mg/Al mixed metal oxides,¹⁴ and hydroxyapatites^{15,16} that were applied in both continuous and batch processes (see also Table S1 and further references). Several mechanistic studies involving these classes of catalysts pointed toward the importance of surface properties, especially acidity and basicity as these influence several key reaction steps, including ethanol dehydrogenation.^{12–14} The balance of acidic and basic sites influences catalytic activity and also product selectivity, since the product 1-butanol can undergo several side reactions, mainly dehydration.^{16,17} Accordingly, a dependence of product selectivity on Mg/Al ratio in hydrotalcite-derived Mg–Al mixed oxides has been observed.^{14,18} In addition to varying the Mg to Al ratio, the composition of Mg–Al mixed

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Scheme 1. Reaction Network for Guerbet Coupling of Ethanol

oxides can be easily modified by introducing additional metal dopants in order to tune their catalytic activity. Although there are some literature examples of doped Mg–Al mixed oxides in the vapor¹⁹ and liquid phases,²⁰ for the Guerbet reaction a highly efficient system has not yet been devised.

In this contribution we describe several novel PMOs derived from synthetic hydrotalcites that do not contain any noble metals. Replacing a small portion of Mg^{2+} in the catalyst structure with Cu and Ni resulted in catalyst compositions that are highly efficient in the Guerbet coupling of ethanol to 1-butanol. The catalysts are robust over several cycles and have been extensively characterized.

■ EXPERIMENTAL PROCEDURE

Catalyst Preparation. The HTC (hydrotalcite) catalyst precursors were prepared by a coprecipitation method, according to literature procedures.^{21,22} In a typical procedure, a solution containing $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (0.06 mol, 12.2 g), $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (0.025 mol, 6.0 g), $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (0.0075 mol, 1.74 g), and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0075 mol, 2.18 g) in deionized water (0.1 L) was slowly added to an aqueous solution (0.15 L) of Na_2CO_3 (0.025 mol, 1 g) at 60 °C under vigorous stirring. The pH was carefully maintained between 9 and 10 by adjusting with frequent additions of an aqueous solution of NaOH (1 M). The mixture was vigorously stirred for 72 h at 60 °C. After cooling to room temperature, the suspension was filtered, and the solid was washed with deionized water and resuspended into a solution of Na_2CO_3 (2 M) which was stirred for 24 h at 40 °C. After the catalyst precursor was filtered, it was washed with deionized water until the washings were chloride-free. The solid was dried at 120 °C overnight, and the hydrotalcite precursor (HTC) was obtained as blue powder (6.68 g). The corresponding copper–nickel-doped porous metal oxide ($\text{Cu}_{10}\text{Ni}_{10}\text{-PMO}$) was obtained after calcining the HTC material at 460 °C for 24 h in air. All porous metal oxides used in this paper were prepared according to the same procedure, replacing a defined amount of Mg^{2+} with Ni^{2+} and/or Cu^{2+} as specified below.

Catalyst Characterization. Powder X-ray analysis was performed on a Bruker XRD diffractometer using Cu K α radiation, and the spectra were recorded in the 2θ angle range 5–70°. Elemental analyses were performed on a PerkinElmer instrument (Optima 7000DV) after full solubilization of the PMO catalysts in aqua regia. The textural characterization was achieved using a conventional nitrogen

adsorption/desorption method, with a Micromeritics ASAP 2420 automatic analyzer. Prior to nitrogen adsorption, the samples were outgassed for 8 h at 250 °C. Surface concentration of acidic and basic sites was determined by using a linear quartz microreactor (l, 200 mm; i.d., 4 mm) in a conventional flow apparatus operating both in continuous and pulse modes. TEM measurements were performed on a Philips CM12 instrument equipped with a high-resolution camera. Powdered samples were dispersed in 2-propanol under ultrasound irradiation, and the resulting suspension was put dropwise on a holey carbon-coated support grid. Elemental distribution was measured in STEM mode on another machine (FEI Tecnai T20 electron microscope) using a HAADF detector and a X-max 80 EDX detector (Oxford instruments). The morphology of the samples was investigated by scanning electron microscopy measurements carried out by using a Philips XL-30-FEG scanning electron microscope at an accelerating voltage of 5–15 kV. Specimens were deposited as powders on aluminum pin flat stubs.

Reaction. In a typical experiment, the catalyst (0.1 g unless otherwise stated) was placed in a Swagelok stainless steel microreactor (10 mL), and ethanol (3 mL) and decane (20 μ L, internal standard) were added. The reactor was sealed and placed in an aluminum block preheated at the desired temperature (note that autogeneous pressure of ca. 80 bar is generated). After the indicated reaction time, the microreactor was cooled down with an ice–water bath and subsequently carefully opened (CAUTION: release of pressurized gases! For more details on the gas phase see [Supporting Information](#), page S3). The liquid sample as well as the catalyst were quantitatively transferred to a 50 mL centrifuge tube. Additional THF was used to wash the reactor and recover all catalyst residues (up to 10 mL total volume). After centrifugation, the solution was transferred into a glass vial and analyzed by GC-FID (Hewlett-Packard 6890 series equipped with a HP-5 capillary column) in order to determine the ethanol conversion and product yields. Compounds were also identified by GC–MS and the injection of pure reference standards for the comparison of retention times in the GC column.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of Porous Metal Oxides. The hydrogen neutral reaction sequence of the Guerbet coupling of ethanol to 1-butanol involves the following key steps: (a) dehydrogenation of ethanol to acetaldehyde, (b) aldol condensation of acetaldehyde including dehydration to

Figure 1. XRD patterns of the synthesized hydrotalcites (left) and the corresponding porous metal oxides (PMOs) after calcination (right).

Table 1. Composition and Textural Properties of PMO Catalysts Prepared

entry	catalyst code	theor composition ^a	exptl composition ^b	surface area (m ² /g)	pore volume (cm ³ /g)	av pore size (nm)
1	MgAl-PMO	Mg _{3.0} Al _{1.0}	Mg _{3.0} Al _{1.0}	233.8	0.91	21.9
2	Ni20-PMO	Ni _{0.6} Mg _{2.4} Al _{1.0}	Ni _{0.6} Mg _{2.1} Al _{1.0}	239.2	0.74	17.6
3	Cu20-PMO	Cu _{0.6} Mg _{2.4} Al _{1.0}	Cu _{0.6} Mg _{2.4} Al _{1.0}	197.7	0.96	21.2
4	Cu10Ni10-PMO	Cu _{0.3} Ni _{0.3} Mg _{2.4} Al _{1.0}	Cu _{0.3} Ni _{0.3} Mg _{2.3} Al _{1.0}	255.7 (120.5) ^c	1.06 (0.67) ^c	17.3 (19.6) ^c

^aBased on quantities of metal ions used during coprecipitation. ^bDetermined by ICP analysis. ^cNumbers in parentheses refer to the catalyst recovered after reaction (catalyst 200 mg, ethanol 3 mL, 310 °C, 6 h).

Figure 2. Screening of different PMO compositions in the Guerbet reaction of ethanol to 1-butanol. Reaction conditions: catalyst (100 mg), ethanol (3 mL), 6 h, 310 °C, decane (20 μ L).

afford the corresponding unsaturated C4 products, and (c) hydrogenation to form saturated longer chain alcohols (Scheme 1).^{7,12} An ideal catalyst should thus possess hydrogenation/dehydrogenation activity in addition to facilitating the aldol-addition and dehydration steps. Previous reports from the literature confirmed the favorable behavior of MgAl-PMO in promoting the self-coupling of ethanol.¹⁴ On the basis of our

previous experiences with Cu-doped PMO in a variety of transformations related to hydrogenation and dehydrogenation of biomass-derived alcohols and polyols,^{21,23} we expected that such catalyst compositions might facilitate the first and last steps of the Guerbet reaction cycle and thus be superior to the common MgAl-PMO. In particular, a facile dehydrogenation step would be beneficial that has been previously proposed to

Table 2. Screening of the Various Prepared PMO Compositions in the Guerbet Reaction of Ethanol to 1-Butanol^a

entry	cat.	conv %	yield %								STY (g _{pro} kg _{cat} ⁻¹ h ⁻¹) ^b	alcohols/ esters
			ButOH	AcOEt	HexOH	OctOH	EButOH	EB	EHexOH	AcOBut		
1	MgAl-PMO	30.8	5.6(83) ^c	0.3	0.6	0.1	0.1	0.1	0.0	0.0	176.3	16.0
2	Cu20-PMO	37.8	5.7(22)	18.1	0.0	0.0	0.0	0.9	0.0	1.0	180.4	0.3
3	Ni20-PMO	30.3	8.8(73)	0.5	1.2	0.1	0.3	0.1	0.0	0.0	278.0	17.3
4	Cu13Ni7-PMO	62.4	18.7(66)	1.5	4.0	0.8	1.0	0.8	0.3	0.5	594.3	8.9
5	Cu7Ni13-PMO	51.2	17.9(72)	0.7	3.8	0.8	0.9	0.6	0.3	0.0	567.8	18.2
6	Cu10Ni10-PMO	47.9	21.1(72)	0.9	4.5	0.7	0.9	0.7	0.4	0.3	670.3	13.8
7 ^d	Cu10Ni10-PMO	47.6	21.7(72)	1.6	4.3	0.6	1.1	0.7	0.2	0.0	670.3	12.1
8	Cu10Ni10-HTC	46.7	17.7(80)	0.8	2.5	0.1	0.8	0.2	0.2	0.0	561.7	21.2

^aReaction conditions: catalysts 0.1 g, ethanol 3 mL, 310 °C, decane 20 μL as internal standard, 6 h. Abbreviations: ButOH, 1-butanol; AcOEt, ethyl acetate; HexOH, 1-hexanol; OctOH, 1-octanol; EButOH, 2-ethylbutanol; EB, ethyl butyrate; EHexOH, 2-ethylhexanol; AcOBut, butyl acetate.

^bSpace-time yield of 1-butanol. ^cNumber in the parentheses is the selectivity of 1-butanol. ^dReaction under Ar.

be rate determining.⁷ Therefore, we set to synthesize a variety of different catalyst compositions to be tested in the Guerbet coupling of ethanol to 1-butanol based on modification of the basic Mg/Al hydrotalcite structure.

First, hydrotalcites (HTC) were synthesized, all containing a small amount of Cu and/or Ni dopant in place of a portion of Mg²⁺ while the M²⁺/M³⁺ ratio was kept at a constant 3:1. The formation of the double-layered structure during HTC synthesis was confirmed by powder XRD measurements (Figure 1, left). These exhibited sharp diffraction peaks at 11.4°, 23.21°, 34.73° and broad reflections at 39.20°, 46.50°, 52.44°, 60.61°, and 61.81° ascribed to the <003>, <006>, <012>, <015>, <018>, <110>, and <113> planes referred to the trigonal hydrotalcite [JCPDS 350965] according to reported data.²⁴

The synthetic HTC samples were subsequently calcined at 460 °C overnight, during which time the lamellar hydrotalcite structure was converted into an amorphous mixed-oxide composition, where a residual Mg(Al)O phase is visible (peaks at 43) whereas no CuO (peaks at 23, 28, and 31) nor NiO oxide phase (peaks at 38, 44, and 64) could be detected (Figure 1, right), indicating a homogeneous dispersion of both active metals. Their composition, determined by ICP analysis, was found to be in very good agreement with the theoretically expected values indicating good incorporation of the metal ions into the parent hydrotalcite structures (Table 1 and Table S3).

The specific surface area of all catalysts, as determined by BET measurements, was comparable within small variations. As shown in Table 1, the addition of Cu slightly decreased the BET to 197.7 m²/g according to a trend observed by other groups,²⁵ while the simultaneous presence of nickel and copper (255.7 m²/g) or nickel alone (239.2 m²/g) did not change significantly the total surface area compared to the reference MgAl-PMO (233.8 m²/g). Also, the pore volume increased for Cu10Ni10-PMO (1.06 cm³/g) compared to the MgAl-PMO catalyst (0.91 cm³/g).

Reactivity of PMO Catalysts in the Guerbet Reaction.

We have started our investigations with comparing the reactivity of the various PMO catalysts at 310 °C for 6 h in a stainless steel batch minireactor. As expected, marked differences in reactivity were seen depending on the nature of the dopant. The results obtained are summarized in Figure 2 and Table 2. With MgAl-PMO, not containing any additional dopants, a 5.6% 1-butanol yield was observed at 30.8% ethanol conversion in 6 h, along with other higher alcohols such as 2-ethyl-hexanol, 1-hexanol, and 1-octanol (Table 2, entry 1). The other large group of products was esters. These esters may be

formed by the dehydrogenation of a possible hemiacetal intermediate that is likely formed under the reaction conditions (see Scheme 1). All of these byproducts can in principle also be used as fuels²⁶ or as blending agents in gasoline.²⁷ Besides alcohols and esters, diethyl ether as well as acetaldehyde, which were formed by dehydration and dehydrogenation reactions, were also detected by GC-MS (see Table S4). Ethylene was detected in the gas phase (Supporting Information, page S3). On the basis of previous research,²⁸ it is known that copper as a dopant could significantly speed up the rate of ethanol dehydrogenation, which is the first step toward the formation of 1-butanol. Indeed, with Cu20-PMO (Table 2, entry 2), ethanol conversion was increased to 37.8%; however, the 1-butanol yield (5.7%) was practically identical to that observed with the MgAl-PMO (Table 2, entry 2 vs 1). This is due to the formation of ethyl acetate as a main product (18.1% yield), which would correspond to a favored dehydrogenation of a possible hemiacetal intermediate.²⁹ The use of nickel only as dopant slightly increased the 1-butanol yield to 8.8% (Table 2, entry 3), but other long chain alcohols remained the main products. The best catalytic performance was achieved with catalysts containing both copper and nickel. The conversion values were increased to 62.4%, 51.2%, and 47.9% (Table 2, entries 4–6), and 1-butanol yield was 18.7%, 17.9%, and 21.1%, respectively (Table 2, entries 4–6). With the increasing amount of Ni dopant besides copper, the selectivity of 1-butanol remained at a constant value of 72%, but the total alcohol to ester ratio increased. The space-time yields with these Cu–Ni PMOs were approximately 3 times higher than those obtained with the composition with no dopants. A control reaction performed under argon atmosphere showed no difference (Table 2, entry 7). The HTC alone was also active, but the yield of 1-butanol was much lower (Table 2, entry 8). To our knowledge, PMO catalysts containing both Ni and Cu dopants have not yet been used for the Guerbet coupling of ethanol. A few examples of similar materials include the hydrogenation of glucose to sorbitol,³⁰ the transesterification of dimethyl oxalate with phenol,³¹ steam reforming reactions,^{32,33} and furfural hydrogenation.³⁴ None of these reports have addressed the influence of the mutual amounts of both dopants in the catalytic outcome. In our study it appears that the ratio between Cu and Ni has an influence on the catalytic performance and the catalyst composition with equimolar amounts of Cu and Ni lead to the best results, 21.1% yield and 72% selectivity of 1-butanol (Table 2, entry 6), among the tested catalysts.

Figure 3. Influence of temperature and catalyst loading on ethanol conversion and distribution of products. Reaction conditions: Cu10Ni10-PMO (50–200 mg), ethanol (3 mL), 6 h, decane (20 μ L).

Figure 4. Product formation profile for the Guerbet reaction of ethanol to 1-butanol for 24 h. Reaction conditions: Cu10Ni10-PMO (100 mg), ethanol (3 mL), 310 $^{\circ}$ C, decane (20 μ L).

Next, this catalyst composition was studied in greater detail. In Figure 3 and Table S5, the dependence of the conversion and yield values on the reaction temperature (in the range 180–320 $^{\circ}$ C) and catalyst loading (ranging from 0.05 to 0.2 g) is shown. As expected, the conversion consistently increased from 2.3% at 180 $^{\circ}$ C to 56.5% at 320 $^{\circ}$ C. At the same time, the yield of 1-butanol increased up to a maximum of 22.2%, and space-time yield reached the outstanding value of 704.6 g $\text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$ at 320 $^{\circ}$ C. However, the carbon balance decreased from 98.5% to 75.0% with the increase of temperature (Table

S3). This is attributed to the formation of volatile byproducts (see also Supporting Information, page S3). It should be noted that the runs at 180 and 220 $^{\circ}$ C take place in the liquid phase, while the reactions at higher temperature are under supercritical conditions, which should facilitate mass transfer. The yield of long chain alcohols rose with the temperature accordingly (Figure 3), whereby the formation of C6+ products (especially C6 and C8 alcohols) at higher temperatures was mainly due to the self-coupling of 1-butanol and to the coupling of 1-butanol with ethanol. That is why the selectivity of 1-

Figure 5. Recycling test. Reaction conditions: Cu10Ni10-PMO (100 mg), ethanol (3 mL), 310 °C, 6 h, decane (20 μ L).

butanol decreased from 78% (Table S5, entry 2 vs 6) to 70%, but the ratio of alcohols to esters rose from 5.9 to 14.1. With increasing catalyst loading, conversion values (62.2%) have improved, but no major changes in the 1-butanol yield took place due to the competing formation of C6 and C8 alcohols (Figure 3).

Next, product formation profiles for 24 h were recorded at 310 °C with 0.1 g of Cu10Ni10-PMO catalyst. As shown in Figure 4, the conversion of ethanol displayed a linear increase up to approximately 10 h, after which no meaningful difference was observed. The yield of 1-butanol reached a constant value of 21% after 6 h. The increase in ethanol conversion in the first 10 h corresponded to the competing conversion of 1-butanol to higher alcohols, especially between 6 and 10 h.

Catalyst Recycling. Recycling experiments using the Cu10Ni10-PMO found good robustness even after seven cycles (Figure 5 and Table S6). The catalyst was recovered at the end of each run, washed with THF and acetone, and reused after drying. A variation in the 1-butanol yield was visible between the first and the second cycles (21% vs 14%) while the relative product distribution remained constant for the subsequent cycles, and the 1-butanol yield stayed in the range 10–14%. The slow decrease in activity after the first cycle was additionally accompanied by an evident reduction of the macroporosity seen from SEM images (Figure 6a,b). These changes were also confirmed by a change in the BET surface area from 255.7 m²/g in the fresh catalyst to 120.5 m²/g after reaction, and a reduction in pore volume from 1.06 to 0.67 cm³/g (Table 1, entry 4).

Furthermore, as shown in the TEM images (Figure 6d), the formation of well-dispersed nanoparticles with a diameter ranging between 20 and 50 nm could be observed, which can be attributed to the formation of active Cu⁰/Ni⁰ species.²⁸ The main difference between the recovered catalyst after the first and the last recycling test (Figure 6d,e) was the partial agglomeration of smaller nanoparticles and the formation of several bigger nanoparticles with a diameter up to 100 nm. This

gradual sintering might be eventually responsible for the reduced catalytic activity, although no major deactivation was apparent after 7 cycles. Additionally, ICP analysis (Table S7) showed almost no leaching of the Cu and Ni incorporated in the catalyst structure while a small amount of Mg and Al loss was observed after the first cycle and almost negligible amounts were detected in the subsequent cycles. This also confirms that the main modification of the catalyst structure takes place after the first cycle and the structure becomes robust during subsequent use.

Structure and Reactivity. The excellent activity of the new Cu10Ni10-PMO catalyst can be attributed to several structural parameters. Both SEM (Figure 6a) and TEM (Figure 6c) measurements of the fresh catalysts showed porous structures that did not display any agglomeration of the copper and nickel dopants, according to a homogeneous dispersion of the transition metals into the catalyst structure. We expected that the simultaneous presence of Cu and Ni may lead to the formation of a Cu–Ni alloy phase during the reaction which could favor the dehydrogenation of ethanol and enhance the stability of the catalyst due to the stronger interaction of both dehydrogenation metals.³⁵ Indeed, elemental mapping (Figure 6h) of a sample collected after the fourth cycle showed the formation of nanoparticles, which contain Cu and Ni. At least one particle in the area shown in Figure 6h indicates the formation of Cu–Ni alloy.³⁶ This was additionally confirmed by the powder XRD pattern of the spent catalyst (Figure S1) collected after the first and fourth cycle with the peaks at 43.0° and 50.9° assigned to the formation of crystalline Cu–Ni alloy regions, as previously also observed by Dalin³³ and Bonura.³⁷

On the basis of previous reports,^{13–15,17,18,24,38–41} an additional parameter markedly influencing reactivity is the acidity and basicity of these catalysts. The distributions of acidic and basic binding sites were determined by temperature-programmed desorption (TPD) of NH₃ and CO₂ for selected different PMO species. The corresponding TPD profiles (Figure S2) and relative numbers of acid (Table S7) and

Figure 6. SEM images of Cu10Ni10-PMO catalyst (a) before and (b) after one reaction and TEM images of Cu10Ni10-PMO catalyst: (c) before reaction; (d) after one reaction; (e, f) after 7 cycles; (g, h) after 4 cycles. Color code refers to the distribution of elements (Cu, red; Ni, green; Mg, blue).

basic sites (Table S9) can be found in the Supporting Information. These measurements found that the MgAl-PMO, not containing any dopants, showed the highest population of strong acidic sites (76%), while the lowest was attributed to the Cu10Ni10-PMO composition (59%). Similarly, the MgAl-PMO catalyst showed the highest basicity while the CO₂ uptake reached a minimum value (0.41 mmol/g_{cat}) for the Cu10Ni10-PMO catalyst. These more balanced acidity and basicity levels compared to the parent MgAl-PMO hint toward a possible correlation between these parameters and reactivity and an influence on the selectivity of 1-butanol. It is interesting that the rate of 1-butanol formation increased linearly with the ratio of base/acid sites (Figure S3).

Coupling of Higher *n*-Alcohols. Finally, the self-coupling of several *n*-alcohols (*n* = 3–6) was attempted in order to observe the influence of the chain length on the extent of dimerization.

The results are displayed in Figure S4. The biggest difference between the reactivity of these alcohols compared to ethanol was the overall lower conversion (below 30%) of the starting material. In the case of 1-propanol, a higher ester/alcohol ratio was observed. In the self-coupling of 1-butanol, 1-pentanol, and 1-hexanol, an even lower substrate conversion was seen. Esters and ethers were obtained as major products, and only a minor amount (<5% yield) of self-coupling product was found. This is in agreement with the persistence of 1-butanol and higher alcohols in the reaction medium when ethanol is used as starting material. Nevertheless, the formation of butyric acid esters and butyl ethers is a major pathway for 1-butanol consumption.

CONCLUSION

In summary, we report herein copper- and nickel-doped porous metal oxide catalysts for the Guerbet coupling of ethanol to 1-butanol. A novel composition containing equimolar amounts of copper and nickel dopants afforded an especially active catalyst that led to 22% 1-butanol yield at 56% ethanol conversion at 320 °C for 6 h, a result that is excellent among the known heterogeneous catalysts. The catalyst has proven robust without significant deactivation over 7 cycles. Structural characterization before and after reaction revealed the formation of metal nanoparticles as well as the existence of a Ni–Cu alloy phase that likely plays a role in the excellent catalytic performance.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02494.

Additional details of the experimental procedures, characterization of catalysts, analysis of products, and comparison of selected examples of heterogeneous catalysts systems (PDF)

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Notes

The authors declare no competing financial interest.

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