

MOF-Derived RuCo Catalyzes the Formation of a Plasticizer Alcohol from Renewable Precursors

Constanze N. Neumann, Steven J. Rozeveld, and Mircea Dincă*

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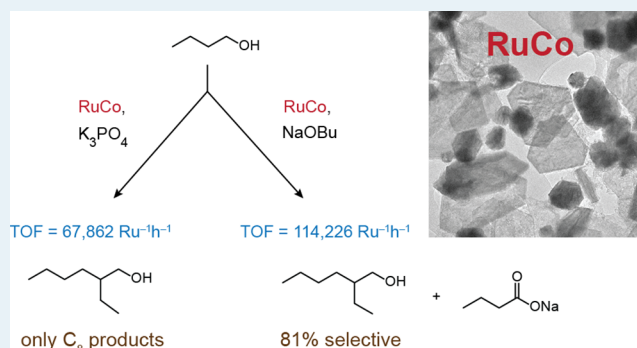
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Supporting Information

ABSTRACT: The Guerbet reaction can be used for the condensation of simple bioalcohols, which simultaneously doubles the carbon count and increases the C:O ratio, to yield valuable commodity chemicals. Here, we report a metal–organic framework (MOF)-derived RuCo catalyst that furnishes 2-ethylhexanol, a plasticizer alcohol currently produced on a 2 Mt/a scale. While the industrial route requires propene, the MOF-derived catalyst uses 1-butanol and delivers turnover numbers up to 1.7×10^6 Ru^{-1} . In combination with K_3PO_4 , it serves as a fully heterogeneous catalyst system that yields the Guerbet alcohol without producing sodium butanoate, a common secondary product from the undesired Cannizzaro reaction.

KEYWORDS: catalysis, metal–organic framework, Guerbet reaction, 2-ethylhexanol, alcohol upgrading, RuCo, 1-butanol, alloy nanoparticle



The synthetic routes toward many commodity chemicals start from fossil fuel-derived precursors and will eventually become challenged, politically and/or economically, because they presuppose a plentiful supply of cheap petrochemical precursors. Although chemicals derived from biomass are promising sustainable building blocks, they differ from the starting materials that many large-scale syntheses are built on. New pathways are needed if petrochemical-derived commodities will be sourced from more sustainable, low carbon count precursors, with C–C bond-forming reactions poised to replace the C–C bond-scission reactions found in cracking processes.^{1–4} Condensation reactions, such as the Guerbet reaction, achieve chain elongation of short-chain oxygenates as well as an increase in the carbon-to-oxygen ratio without implicating CO_2 formation.^{1,4,5}

Indeed, modification of synthetic strategies toward commodity chemicals to incorporate biomass feedstock need not render them more cumbersome. For example, 2-ethylhexanol, which is manufactured on a larger scale than any other alcohol containing more than four carbons, is currently accessed from propene via a three-step sequence involving hydroformylation, aldol condensation, and hydrogenation (Figure 1).^{6,7} Alternatively, 2-ethylhexanol could be produced from biomass-derived ethanol via two subsequent Guerbet reactions if sufficiently active and selective catalysts are available.^{8,9}

Because the production of transportation fuels is the largest-scale application of oil-derived products, the synthesis of biofuel alternatives to gasoline, diesel, and jet fuel is a pivotal area for the use of bioalcohols. Consequently, the upgrading of ethanol to the gasoline alternative 1-butanol has been an

overwhelming focus of recent research activity on catalysts for the Guerbet reaction,^{10–16} with developments in the upgrading of higher alcohols lagging behind.^{17–19} However, a transition to wide-spread use of biofuels is complicated by the enormous production scales required and the fact that gasoline and diesel are replaced by novel materials. With comparatively smaller production scales and the synthesis of an identical product, commodity chemical synthesis from renewable materials via Guerbet chemistry could serve as a stepping stone for biofuel production from biomass. Although currently available catalysts for the Guerbet reaction of C_{3+} alcohols generally display good selectivity for the desired alcohol product, low catalyst activity is still prevalent.^{5,7,20,21} Notable exceptions are the iridium-catalyzed butanol upgrading mediated by NaOH in water,²² whose turnover frequency (TOF) of $63 \text{ Ir}^{-1} \text{ h}^{-1}$ and 98% selectivity may facilitate upgrading of fermentation-derived butanol, as well as the recently reported butanol-upgrading reaction over $\text{Ni}/\text{Ca}_x\text{Mg}_y\text{O}$.²³

In our own efforts to develop an efficient and selective catalyst for upgrading ethanol to 1-butanol, we found that simple ruthenium compounds supported on a suitable metal–organic framework (MOF) yield highly active RuNi-alloy

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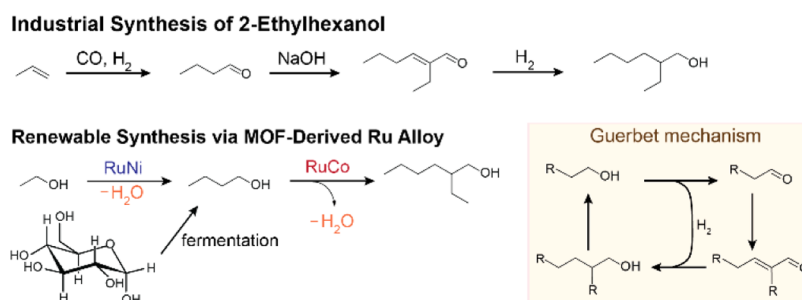


Figure 1. 2-Ethylhexanol, the precursor to the plasticizer diester bis(2-ethylhexyl) phthalate, can be derived from renewable materials via two successive Guerbet reactions catalyzed by metal–organic framework (MOF)-derived Ru alloy nanoparticles.

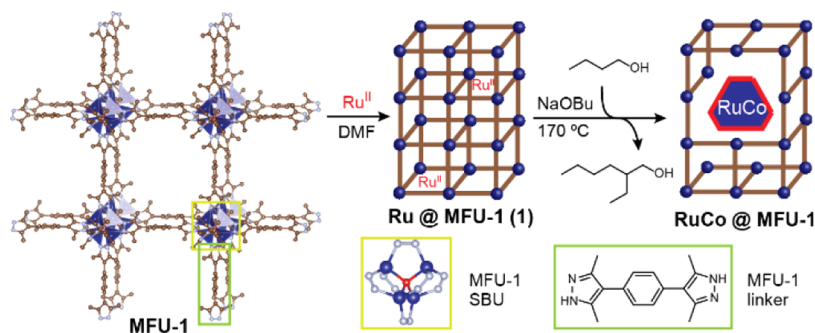


Figure 2. Schematic representation of the synthesis of **1** and its conversion to the catalytically active species under the Guerbet reaction conditions.

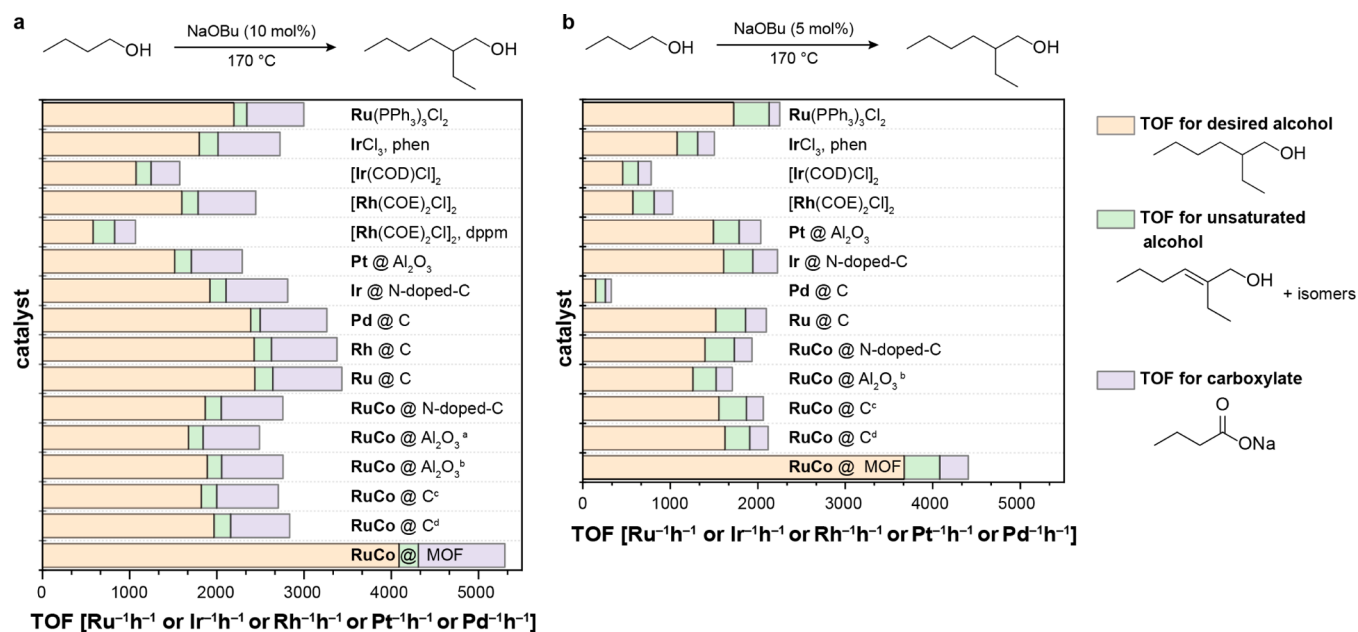


Figure 3. Comparison of catalytic performance of different Guerbet catalysts in butanol upgrading in the presence of 10 (a) or 5 mol % (b) NaOBu at 170 °C [phen = phenanthroline and dppm = bis(diphenylphosphino)methane].^{7,21,22,26,27,29,30} The overall TOF was color-coded according to the fraction of 1-butanol converted into the respective reaction products. Loading of Ru on catalyst supports (in wt %) ^a0.2 ^b1.8 ^c3.4 ^d1.1 (see Figures S20–S21 and Tables S3–S4 for details).

nanoparticle catalysts when subjected to the reducing reaction conditions of the Guerbet reaction (Figure 1).¹⁶ However, the formation of 1-butanol via the Guerbet reaction with high selectivity requires a catalyst that shows very limited activity for the Guerbet reaction of 1-butanol so that MOF-derived RuNi is not a suitable catalyst for the production of 2-ethylhexanol. Given the compositional and structural diversity of MOFs, we set out to investigate if the in situ alloy formation between pore-incorporated ruthenium compounds and metals con-

stituting MOF secondary building units (SBUs) could be generalized in order to access highly active Guerbet catalysts displaying complementary starting material selectivity relative to RuNi@MOF and thus be amenable to furnish high-volume chemicals such as 2-ethylhexanol from renewable precursors (Figure 1).

To this end, we were pleased to find that the cobalt-based MOF Co^{II}O(1,4-bis[(3,5-dimethyl)pyrazol-4-yl]-benzene)₆ (MFU-1)^{24,25} can, after pore incorporation of a commercially

Table 1. Alcohol Upgrading Catalyzed by **1** Conducted in a Stainless-Steel Pressure Reactor at 170 °C

conditions	Activity		selectivity			Con ^g	[Ru] ^h	comment
	TON ^a	TOF ^b	G ^c	U ^d	C ^{e,f}			
1 optimized conditions	1,770,504	114,226	0.81	0.11	0.08	0.31	3.30 × 10 ⁻⁵	COD, 5 mol %, 15.5 h ⁱ
2 catalyst reuse (# 1)	1,047,086	67,554	0.71	0.19	0.10	0.14	3.30 × 10 ⁻⁵	TOF ratio = 0.59 ^j
3 #1 with NaOBu replaced by K ₃ PO ₄	1,051,859	67,862	0.80	0.16 ^k	n.d.	0.20	3.30 × 10 ⁻⁵	TOF ratio = 0.59 ^j
4 #1 with NaOBu replaced by LiOH	395,854	25,539	0.53	0.36 ^k	n.d.	0.06	3.30 × 10 ⁻⁵	TOF ratio = 0.22 ^j
5 targeting higher 2-ethylhexanol selectivity	193,652	10,758	0.86	0.07	0.06	0.28	2.75 × 10 ⁻⁴	nbd, 2.5 mol % 18 h ^f
6 targeting more rapid 1-butanol conversion	305,642	21,832	0.76	0.05	0.19	0.39	2.75 × 10 ⁻⁴	COD, 10 mol %, 14 h ^f
7 #1 with increased catalyst loading	237,713	15,336	0.84	0.05	0.11	0.27	2.75 × 10 ⁻⁴	COD, 5 mol %, 15.5 h ⁱ
8 catalyst reuse (# 7)	150,303	9697	0.72	0.16	0.12	0.19	2.75 × 10 ⁻⁴	TOF ratio = 0.63 ^j
9 #7 with NaOBu replaced by NaOH	119,453	7707	0.69	0.16	0.15	0.16	2.75 × 10 ⁻⁴	TOF ratio = 0.50 ^j
10 #7 with NaOBu replaced by K ₃ PO ₄	129,614	8362	0.78	0.17 ^k	n.d.	0.21	2.75 × 10 ⁻⁴	TOF ratio = 0.55 ^j

^aTurnover number [Ru⁻¹]. ^b[Ru⁻¹ h⁻¹]. ^cSelectivity for the desired Guerbet alcohol. ^dSelectivity for the unsaturated Guerbet alcohol. ^eSelectivity for sodium carboxylate. ^fn.d. = not detected. ^gConversion. ^hAmount of ruthenium present in the reaction mixture [mmoles]. ⁱAlkene ligand on a ruthenium precursor, concentration of base promoter, and reaction time. ^jComparison of TOF with an analogous experiment using a pristine catalyst and alkoxide promoter. ^k(Unsaturated) C₈ aldehyde formed (Figure S28). See Supporting Information for detailed reaction conditions and results.

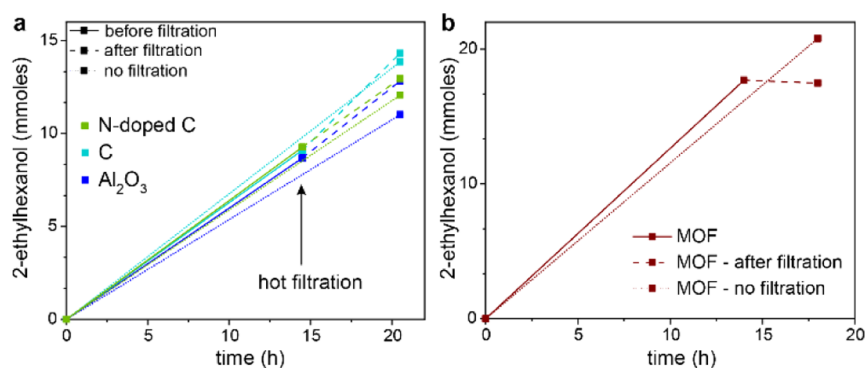


Figure 4. Hot filtration results for RuCo catalysts supported on classic support materials (a) and derived from Ru-doped cobalt MOFs (b) (see Table S7).

available ruthenium complex, give rise to a highly active catalyst for the upgrading of 1-butanol (Figures 2, S1–S10). No cobalt removal was detected after soaking MFU-1 with a suspension of Ru(nbd)Cl₂ (nbd = norbornadiene) in DMF, and the structural integrity (Figures S2 and S8) of MFU-1 was maintained, as verified by powder X-ray diffraction (PXRD). The surface area of the MOF decreased from 1441 to 881 m² g⁻¹ (Figure S6) during incorporation of the ruthenium salt. Ru@MFU-1 (**1**) was thus assumed to consist of Ru(nbd)Cl₂ trapped inside the pores of the MFU-1 or attached to the MOF without replacement of cobalt (Figure 2).

Given the broad range of reaction conditions and catalysis metrics used in the literature, we synthesized or purchased previously reported catalysts for the Guerbet reactions of 1-butanol or 1-pentanol to benchmark the activity of **1** through direct side-by-side comparison (Table S1, Figure S11).^{7,21,22,26,27} All Guerbet reactions were conducted neat to maximize space time yield and minimize solvent waste. Due to the privileged status of alkoxide bases in Guerbet reactions,^{7,10,11,16,20,21,28} two different concentrations of NaOBu (10 mol %: Figure 3a and 5 mol %: Figure 3b) were chosen to compare the catalysts using a constant concentration of active metal species at 170 °C. Because the activity of catalyst **1** easily surpassed those of all other published Guerbet catalysts tested, we further prepared RuCo nanoparticles, the presumed active species formed in situ from **1** (Figure 2), supported on traditional solid supports of

different polarities (Table S2, Figures S12–S19). RuCo nanoparticles on carbon, N-doped carbon, and alumina furnished comparable activities to other, more expensive, metal active species, but the choice of metal components did not, in itself, account for the superior activity of **1** (Figure 3).

In addition to the desired Guerbet product (Figure 3, orange bars), unsaturated C₈ alcohols (Figure 3, blue bars) and sodium butyrate (Figure 3, green bars) were observed for all catalysts studied, with **1** showing the highest selectivity for the desired Guerbet product 2-ethylhexanol. Although a decrease in the amount of base promoter from 10 to 5 mol % reduced the fraction of 1-butanol converted to sodium butyrate via the undesired Cannizzaro or Tishchenko reactions for all catalysts, this also caused an increase in the fraction converted to unsaturated alcohols. However, for **1**, the increase in unsaturated alcohol formation upon reducing the amount of base promoter was less-pronounced, from 4% (average of other catalysts: 8%) to 9% (average of other catalysts: 19%).

Encouraged by the outstanding catalytic performance of **1** for butanol upgrading, we set out to investigate the effect of ruthenium loading on the MFU-1 support as well as the effect of the total amount of ruthenium present in the reaction mixture (Table 1). The in-situ formation of the active catalyst rendered it likely that high-dilution conditions engendered by very low catalyst loading could lead to high catalyst performance, on a per-Ru basis. We indeed found that irrespective of the ruthenium alkene precursor (either

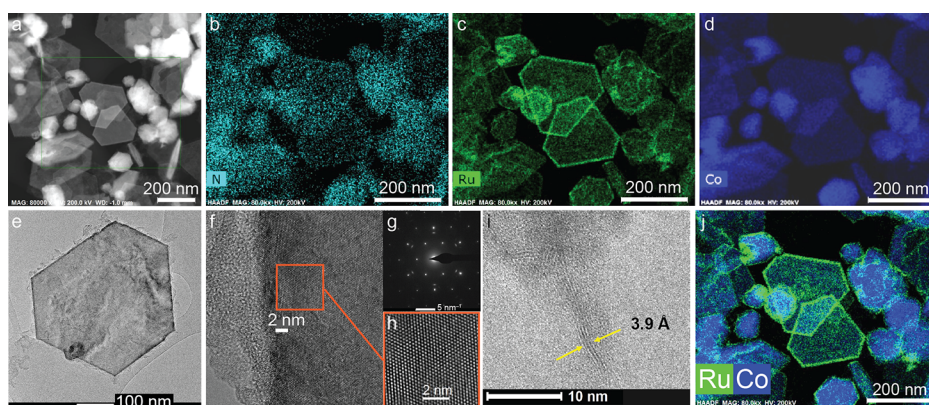


Figure 5. STEM image (a), TEM images (e, f, h, i), fast Fourier transform (g), and EDS mapping for N (b), Ru (c), and Co (d, j) of RuCo formed in butanol-upgrading reactions with **1** in the presence of 5 mol % NaOBU.

Ru(nbd)Cl₂, nbd = norbornadiene, or Ru(COD)Cl₂, COD = cyclooctadiene) used to generate **1**, or the amount of base cocatalyst, the catalytic performance on a per-Ru basis improved considerably with decreasing concentration of Ru (at a constant Co:Ru ratio), with only minimal effect on the conversion (Figure S22, Tables S5–S6). Crucially, turnover numbers exceeded 1.7×10^6 on a per-ruthenium basis, while the selectivity for the formation of the desired Guerbet alcohol exceeded 80% (Table 1, entry 1).

Although we had previously observed a very strong dependence on the Ru:Ni ratio in the synthesis of MOF-derived RuNi catalysts for ethanol upgrading, the performance of **1** did not display a strong dependence on the loading of ruthenium on the cobalt-based MFU-1 support (Table S6).¹⁶ However, loadings of Ru should be kept below around 2% relative to cobalt to prevent leaching of the catalytically active species (Figure S23–S24 and Table S7).

Hot filtration experiments for butanol-upgrading reactions in the presence of 10 mol % NaOBU showed that the catalytic activity of the filtrate was partially retained (Figure S25), and inductively coupled plasma–mass spectrometry analysis indicated leaching of 1% of the cobalt content and 5% of the ruthenium content of **1** into the reaction mixture (Table S8). Reducing the amount of base promoter to 5 mol %, and use of precatalyst with a Ru:Co ratio below 2%, ensured that the catalytically active species was entirely retained by the support material, with no catalytic activity observed in the filtrate (Figure 4b). Hot filtration experiments with classic supports containing low Ru loadings (carbon: 1.1 wt %, Al₂O₃: 1.8 wt %, and N-doped carbon: 0.3 wt %, Figure 4a, Table S7) in the presence of 5 mol % NaOBU led to extensive leaching of the catalytically active species, in line with what has been described for Pd/C and Pt/Al₂O₃.^{7,27}

No volatile side products could be detected in the headspace of the reactor other than H₂ (Figure S27) formed alongside sodium butanoate in the Cannizzaro side reaction (Figure S26). Mass balance calculations accounted for >95% (>98% in most cases) of the mass in all reactions catalyzed by **1** (Figure S26–29 and Tables S3–4). Recovered **1** could be reused after separation from the reaction mixture via filtration and washing with water and acetone. Recovered batches of the catalyst yielded ~60% of the originally observed activity (Table 1, entries 2 and 8). The minute amounts of the catalyst required, in combination with the small size of some of the catalyst particles, however, rendered efficient catalyst recovery for

recycling studies operationally challenging, which likely contributed to the apparent decrease in activity upon catalyst reuse (see Supporting Information for detailed discussion).

Intrigued by the significantly higher catalytic activity of **1** compared to RuCo nanoparticles supported on alumina, carbon, or N-doped carbon, we obtained high-resolution transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM), and energy-dispersive X-ray spectroscopy (EDS) mapping data for RuCo particles recovered from butanol-upgrading reactions conducted under optimized reaction conditions (Figures 5 and S30–S31). We observed, in addition to spherical CoO_x particles coated with ruthenium, crystalline truncated triangular CoO_x particles with an edge length of approximately 200 nm (Figure 5e) and a thickness of 0.39 nm (Figure 5i). High-resolution TEM imaging (Figure 5f,h) and selected area diffraction (Figure 5g) show that the nanoplates formed are crystalline. Interestingly, the outer edges of particles of both morphologies appear to be highly enriched in ruthenium, rendering the fraction of ruthenium atoms accessible to substrates comparable to what would be observed with nanostructures of very small diameter.

We attribute the high stability under forcing conditions and the enhanced catalytic activity of Ru@MFU-1-derived RuCo compared to other support materials to the formation of large stable CoO_x nanoparticles and the positioning of catalytically active ruthenium centers on high-energy surface sites (Figures S32–S36 and Tables S9, S10).^{5,31}

Replacement of NaOBU with K₂CO₃ as a base promoter in butanol-upgrading reactions catalyzed by **1** only yielded small quantities of saturated and unsaturated C₈ aldehydes.³² PXRD analysis of the recovered catalyst showed that the MOF support remained crystalline and RuCo formation was not observed in the presence of K₂CO₃ (Figure S37), which suggests that in situ nanoparticle formation is crucial to catalyst activity.

Moreover, we observed an increase in the catalytic activity per-ruthenium center as the concentration of the catalyst was reduced, with consistent values being observed for initial ruthenium concentrations below 2.8×10^{-4} mmol (Figure S22). Tripling the amount of catalyst used led to a roughly fourfold decrease in the per-ruthenium activity in the presence of either 10% mol or 2.5 mol % base promoter (Tables S5, S6). We attribute the variation in per-ruthenium activity to the in situ formation of catalysts with different kinetic profiles depending on the concentration of precatalyst, highlighting

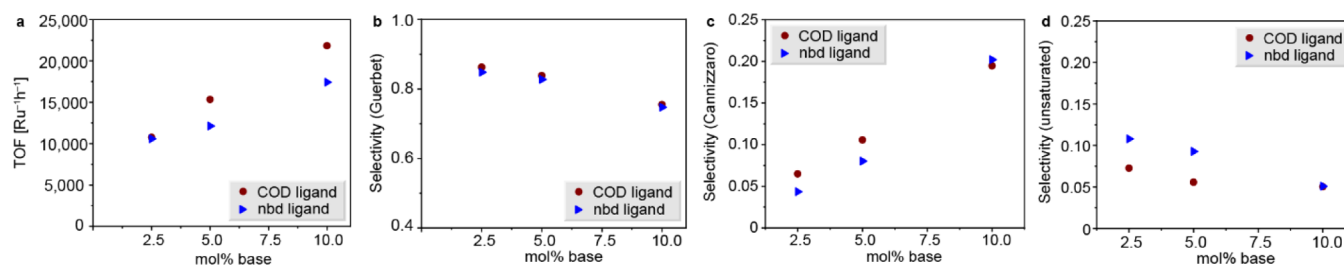


Figure 6. Variation of TOF (a) and selectivity for 2-ethylhexanol (b), sodium butanoate (c), and unsaturated C₈ product (d) with the concentration of NaOBu cocatalyst, and use of Ru(nbd)Cl₂ versus Ru(COD)Cl₂ to generate **1** ([Ru] = 2.75 × 10⁻⁴ mmol, 20.0 mL 1-butanol, 170 °C, 15.5 h). See Supporting Information for detailed reaction conditions and results.

the practical importance of further study of the in situ active catalyst formation process.

As previously observed with RuNi-catalyzed ethanol upgrading, a trade-off exists between the catalytic activity and the selectivity for the formation of the desired Guerbet alcohol because both variables depend on the identity and the amount of the base promoter used (Figure 6).¹⁶ Water, which is formed in an equimolar amount to the alcohol product in Guerbet reactions, causes gradual hydrolysis of the sodium alkoxide promoter to NaOH with increasing conversion, which leads to loss of activity in many Guerbet systems.^{7,21} Gratifyingly, butanol upgrading with **1** proceeds efficiently (TOF = 7707 Ru⁻¹ h⁻¹) even when NaOH is used as the exclusive promoter, although both the catalyst activity and selectivity for Guerbet alcohols is affected by the change in the base promoter (Table 1, entry 9).

The formation of carboxylate side products is commonly attributed to the presence of NaOH formed via hydrolysis of the alkoxide promoter.^{4,21} Consequently, continuous water removal would not only lead to higher conversions of starting alcohol being readily accessible but may also increase the overall selectivity of the reaction.^{21,33} Alternatively, the formation of carboxylate side products, which lead to consumption of the starting material as well as the base cocatalyst, could be eliminated using bases that are virtually insoluble in the reaction medium, such as K₃PO₄ or LiOH (Figures S38 and S39).^{4,12,33} The cost of replacing sodium alkoxides necessitated by the loss of the base promoter through conversion to sodium carboxylates that are unable to promote the Guerbet reaction impedes further development of Guerbet reactions that achieve efficient alcohol upgrading below 200 °C via synergistic base and transition-metal catalysis.

Gratifyingly, no carboxylate salt formation was detected in 1-butanol upgrading with **1** in the presence of 5 mol % K₃PO₄, whereas 55–59% of the optimized catalytic activity for butanol upgrading achieved with NaOBu was retained (TON up to 1,007,268 Ru⁻¹; see Table 1, entries 3 and 10). Avoiding the Cannizzaro side reaction and the formation of undesired butyric acid is necessary to permit recycling of both **1** and K₃PO₄ because butyric acid consumes an equivalent of the basic cocatalyst and yields sodium butyrate, which is not an active promoter for the Guerbet reaction (Figure S39). Reuse of the entire catalytic system furnished TOF = 30,309 Ru⁻¹ h⁻¹ (45% of the original catalytic activity) with reduced selectivity for the saturated Guerbet product (Table S11), lending promise that efficient recycling of both catalyst and base may be possible with process improvement for catalyst recovery and/or reactivation conditions.

CONCLUSIONS

We have shown that a new, MOF-derived RuCo nanoparticulate catalyst is efficient (TON > 10⁶ Ru⁻¹) and selective for the upgrading of 1-butanol into the commercially important plasticizer alcohol 2-ethylhexanol. Catalytically active RuCo particles can be obtained in situ from air-stable, easily accessible Ru@MOF precatalysts and are retained more effectively on the MOF support than on traditional supports such as (N-doped) carbon or alumina. Replacement of the ubiquitous base promoter NaOBu with K₃PO₄ ensures the efficient formation of 2-ethylhexanol without simultaneous production of undesired carboxylate salts.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.1c01391>.

Further experimental details, synthetic procedures for catalysts, and electron microscopy images (PDF)

AUTHOR INFORMATION

Corresponding Author

Mircea Dincă – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; orcid.org/0000-0002-1262-1264; Email: mdinca@mit.edu

Authors

Constanze N. Neumann – Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States; Present Address: Department of Heterogeneous Catalysis, Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim, Germany.; orcid.org/0000-0003-1004-1140

Steven J. Rozeveld – Core R&D, The Dow Chemical Company, Midland, Michigan 48674, United States

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acscatal.1c01391>

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Notes

The authors declare no competing financial interest.

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