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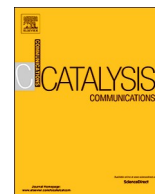
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Short communication

Activity of heterogeneous supported Cu and Ru catalysts in acceptor-less alcohol dehydrogenation

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ABSTRACT

Acceptor-less alcohol dehydrogenation reaction allows the co-production of added-value carbonyl compounds and H₂ from alcohols. Focusing on supported Ru and Cu catalysts, we evaluated the support effect on the dehydrogenation of 2-octanol and 1-octanol and identified the side products as resulting from aldolisation coupling. The most active and selective catalysts were then tested on the aliphatic vicinal-diol octan-1,2-diol and the highest conversion was reached using Cu/ZrO₂ (60%) with a high selectivity (94%) towards 1-hydroxy-2-octanone.

1. Introduction

Acceptor-less alcohol dehydrogenation (AAD) reaction allows the coproduction of carbonyl compound and hydrogen, which find applications in chemical industries and for energy uses. Various heterogeneous catalysts can be used to promote AAD reaction, including supported noble (i.e. Pt [1], Pd [2], Ru [3–5], Au [6–8] and Ag [9–13]) and non-noble (i.e. Cu [14–16], Ni [17,18], and Co [19–22]) metal catalysts. In general Ru and Cu catalysts are of great interest. Ru is a noble metal known for its good catalytic activity in many reactions, even with small loading, specifically in aqueous phase [23,24], whereas Cu is considered as a potential replacement for the more expensive precious metals, but often it must be used in large quantities and in organic solvent [25]. Ru [3–5] and Cu [14–16] catalysts have already been proved active in dehydrogenation of some primary and secondary aliphatic and aromatic monoalcohols.

Besides the choice of the metallic phase, the choice of the support is also critical, especially in the case of the AAD reaction, which is believed to take place at the interface between support and metal nanoparticles (NPs) [17]. Acid-basic sites of support can assist the O–H bond dissociation, while the C–H bond scission occurs on metal NPs. As it appears from the literature, NPs size and the nature of the support are indeed decisive for the catalysts activity. For example, it was shown by Chen et al. [8] that the smaller was the size of Au NPs, the more active was the catalyst. However, the optimal support depends on the metal. Cu on hydrotalcite (HT) exhibited better activity and selectivity than

for example Cu/Al₂O₃ and Cu/TiO₂ in dehydrogenation of secondary alcohols [14]. It seems that in case of Ru catalysts the support effect has not been considered up to now.

Seeking a high activity should not be at the expense of a high selectivity towards the targeted product (here a carbonyl). When using Cu and Ru supported catalysts, some by-products were observed, but rarely identified. With Ru/AlOOH, Kim et al. [4] mentioned the formation of by-products during 1-octanol dehydrogenation, but without exact determination. Using Cu/HT, Mitsudome et al. [14] reported the formation of benzyl benzoate during benzyl alcohol dehydrogenation, and of aldol product during cyclopentanol dehydrogenation. Therefore, this aspect requires further investigations, as it may be alcohol and/or catalyst dependent [26,27] and will be critical when moving from simple alcohol to polyols, as the ones derived from biomass (glycerol, sorbitol, etc.).

As a first step towards polyols, the dehydrogenation of diols is of great interest, but until now the reports are scarce [4,13,28,29]. Dehydrogenation of vicinal diols, containing two secondary hydroxyl groups, resulted in formation of α -hydroxyketones as the main reaction products [28,29]. Dehydrogenation of diols with two primary terminal hydroxyl group led to lactones [4]. Up to now, only Guicheret et al. [28] examined a diol with both primary and secondary hydroxyl groups. In the latter paper, Ni/SiO₂ exhibited low conversion (25%) and some chemoselectivity (60%) towards secondary OH group dehydrogenation. Thus a better performing catalyst is still sought. To the best of our knowledge, neither Cu, nor Ru have been tested yet towards

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the dehydrogenation of diol containing primary and secondary hydroxyl groups.

In this work, the performance of Cu and Ru supported catalysts were examined in acceptor-less alcohol dehydrogenation reactions. At first, the support effect was investigated for both metals in the reaction with model secondary linear aliphatic alcohol, namely 2-octanol, along with a careful identification of the side products. And subsequently, the most efficient catalysts were tested in the dehydrogenation of primary alcohol (1-octanol) and diol (1,2-octanediol).

2. Experimental

2.1. Catalyst synthesis

5 g of Cu (5 wt%) and Ru (1 wt%) catalysts were prepared by wet impregnation of TiO₂ (DT51D, 85 m² g⁻¹, Tronox), ZrO₂ (137 m² g⁻¹, MEL Chemicals), C (L3S, 1095 m² g⁻¹, CECA ARKEMA), γ -Al₂O₃ (119 m² g⁻¹, Degussa) and ZnO (16 m² g⁻¹, Alfa Aesar) with an aqueous solution of Cu(NO₃)₂ · xH₂O (0.35 mol L⁻¹) or Ru(NO)(NO₃)₃ (0.15 mol L⁻¹).

The support was dispersed in the appropriate volume of deionized water. After addition of the metal precursor, the suspension (total volume 100 mL) was stirred for 2 h (600 rpm, RT) and evaporated. The solid was dried overnight (N₂ flow, 80 °C) and crushed. The sample was then reduced in H₂ flow (50 mL min⁻¹, 2 °C min⁻¹, 300 °C, 3 h), cooled down, flushed with Ar (50 mL min⁻¹, 10 min) and passivated in 1% v/v O₂/N₂ (50 mL min⁻¹, room temperature, 0.5 h).

2.2. Catalyst characterization

Inductively coupled plasma – optical emission spectroscopy (ICP-OES) analysis was used to determine the Cu and Ru loadings (details in Supplemental section) and to measure the concentration of Cu in the Cu(NO₃)₂ · xH₂O water solution. Powder X-ray diffraction (XRD) patterns were registered using a BRUKER Advance D8A25 diffractometer, equipped with a CuK α radiation source ($\lambda_{K\alpha} = 1.54184 \text{ \AA}$), a nickel filter, and a multi-channel fast detector LynxEye. The scans were recorded in the range $5^\circ < 2\theta < 80^\circ$ at $0.04^\circ \text{ s}^{-1}$. When possible, the Scherrer equation was applied to calculate the crystallite size. Transmission Electron Microscopy (TEM) images were obtained using a JEOL 2010 apparatus, operating at an acceleration voltage of 200 kV, and equipped with an EDX (Energy Dispersive Spectroscopy) detector.

2.3. Catalysis procedure

Some features of the operating conditions and the analysis are given below, but more details can be found in Supplemental section or elsewhere [21]. Catalytic tests were performed in a semi-batch glass reactor at 145 °C, under inert atmosphere (10% v/v N₂/Ar, 30 mL min⁻¹), and with stirring (750 rpm). 0.5 g of catalyst was employed for 1-octanol and 2-octanol (0.8 mol% of Cu or 0.1 mol% of Ru), and 1.0 g of catalyst was used for 1,2-octanediol (1.6 mol% of Cu and 0.2 mol% of Ru).

The catalyst and 30 mL of decane were introduced into the reactor and heated up to 145 °C. When the given temperature was reached, the substrate solubilized as a solution in decane was added to the reactor ($V_{\text{total}} = 45 \text{ mL}$; $C_{\text{alcohol}} = 0.95 \text{ mol L}^{-1}$) - the catalytic experiment was started and performed for 24 h. After reaction, Cu/ZrO₂ was recovered by filtration, washed with ethanol, and dried overnight at 80 °C under N₂ flow. The collected material was further used in a second run for 1,2-octanediol dehydrogenation, after re-activation by in situ H₂ pre-treatment [21].

The outlet gases from the reactor were analysed using a gas chromatograph Shimadzu GC-2010, equipped with Supelco Carboxen-1010 PLOT column and TCD detector. Liquid samples, collected periodically during the reaction, were analysed using a gas chromatograph Shimadzu GC-2010, equipped with ZB-FFAP column and FID detector.

Table 1

ICP-OES and XRD characterization data for Cu and Ru supported catalysts.

Catalyst	Cu (wt %)	XRD – crystallite size (nm)	SA ^a (m ² g ⁻¹)	Catalyst	Ru (wt %)	XRD – crystallite size (nm)
Cu/TiO ₂	4.3	63	85	Ru/TiO ₂	1.1	< 5
Cu/ZrO ₂	4.4	< 15	137	Ru/ZrO ₂	1.2	< 5
Cu/C	4.2	40	1095	Ru/C	1.1	< 5
Cu/ γ -Al ₂ O ₃	4.6	33	119	Ru/ γ -Al ₂ O ₃	1.1	< 5
Cu/ZnO	4.6	34	16	Ru/ZnO	1.1	< 5

^a Specific surface area of the supports, determined by N₂ physisorption

An Agilent 6890 N gas chromatograph (GC) with ZOEEX cryogenic modulation system (equipped with ZB5 and VF17 columns), and coupled with MS Agilent 5975B mass spectra detector, was used to identify the reaction by-products. Conversion of the substrate X (%), selectivity in desired C8 carbonyl compound S_{C8} (%), C16 compounds S_{C16} (%), and C24 compounds S_{C24} (%), yields in C8 carbonyl compound Y_{C8} (%) and in hydrogen Υ_{H_2} (%), are defined in Supplemental section. Blank experiments were conducted over the bare supports (TiO₂, ZrO₂, C, Al₂O₃, ZnO) and less than 3% of conversion were observed after 24 h.

3. Results and discussion

3.1. Characterization

Table 1 summarizes the ICP-OES, the surface area and XRD analyses of the supported Cu and Ru catalysts. The elemental analysis revealed that the actual loading for Cu and Ru catalysts are around 4.5 wt% and 1.1%, respectively.

The diffractograms obtained by XRD analysis are presented in Fig. A.1. in Supplemental section, and, the main crystallite sizes are gathered in Table 1. For Cu catalysts, the peaks at $2\theta = 43.3^\circ$, 50.4° and 74.1° can be assigned to the (111), (200) and (220) planes of fcc metallic Cu. The signals are visible for all the Cu catalysts (main crystallite sizes over 30 nm), except for Cu/ZrO₂ where the metal crystallites must be smaller (< 15 nm). Ru exhibit hcp crystallographic phase, for which the main signal is expected at $2\theta = 44.4^\circ$ ((101) plane). However, it is not visible for any of the Ru supported catalysts, which implies small mean metal crystallite sizes (< 5 nm), as confirmed by CO chemisorption (Table A.1).

TEM analysis was conducted on Cu/ZrO₂ and Ru/ZrO₂ in order to investigate the size distribution of metal NPs. Yet, due to the low contrast between the support and the metals it was not possible to distinguish the nanoparticles, although EDX analyses confirm the presence of metals (Fig. A.2).

3.2. Activity results

3.2.1. Support effect

In the present study the aim was to assess the effect of the support in alcohol dehydrogenation reactions for Cu and Ru catalysts. Five supports of different nature were used: amphoteric (TiO₂, ZrO₂ and γ -Al₂O₃), neutral (C), and basic (ZnO). The catalysts were tested towards 2-octanol dehydrogenation, and the corresponding results are collected in Table 2.

All Cu and Ru catalysts occurred to be active towards alcohol dehydrogenation, and concomitant production of gaseous H₂ was registered, proving the adopted acceptor-less mechanism. The most active Cu catalyst was Cu/ZrO₂ (amphoteric support), for which the conversion of alcohol was complete after 24 h. It was followed in activity by Cu/C (neutral carrier), and Cu/ZnO (basic support). For the three catalysts, the selectivity to 2-octanone was above 98% at 30% conversion. However after 24 h, the selectivity was only of 7% for Cu/ZrO₂, while it was almost quantitative for the other catalysts. The conversion and

Table 2

Dehydrogenation of 2-octanol in the presence of Cu and Ru catalysts. Reaction conditions: 0.5 g of catalyst (0.8 mol% of Cu or 0.1 mol% of Ru), 2-octanol (0.95 mol L⁻¹), decane, 24 h, 145 °C, V_{total} = 45 mL.

Catalyst	X (%) ^a	S _{30%} (%) ^b	S _{C8} (%) ^a	Y _{C8} (%) ^a	Y _{H₂} (%) ^a
Cu/TiO ₂	2	n.a.	n.a.	2	0
Cu/ZrO ₂	> 99.9	99.7	7	7	92
Cu/C	73	98	98	69	62
Cu/γ-Al ₂ O ₃	16	n.a.	98	16	14
Cu/ZnO	52	> 99.9	99.8	52	50
Ru/TiO ₂	72	99.9	96	69	72
Ru/ZrO ₂	83	> 99.9	71	59	73
Ru/C	43	98	97	42	40
Ru/γ-Al ₂ O ₃	30	99.9	99.9	30	27
Ru/ZnO	16	n.a.	> 99.9	16	14

n.a. – not applicable.

^a After 24 h.

^b Selectivity to 2-octanone (C8) at 30% of conversion.

yield of products as a function of time are presented in Fig. 1 for Cu/ZrO₂. At the beginning of the reaction, 2-octanone and H₂ were produced in equimolar ratio. When the conversion reached ~70% the formation of C16 and C24 by-products was detected. The C16 by-products are formed by aldol condensation reaction, as reported with Co catalysts [21]. GC–MS analysis was performed to identify the C24 by-products (example of mass spectra in Fig. A.3). They appeared to be a mixture of diastereomers formed by further aldol condensation reaction. The small discrepancies between conversion and yield of H₂ suggest sequential hydrogenation of the C16 and C24 by-products. The main reaction pathway associated with 2-octanol reactivity is proposed in Fig. 2 (plain arrows). The figure also includes other possible molecules formed via aldolisation, but less likely due to steric hindrance (dashed arrows).

In line with the literature [14], the use of amphoteric support seems to be beneficial for Cu catalyst. Mitsudome et al. reported higher conversion with Cu/Al₂O₃ (96%) and Cu/TiO₂ (42%), however the reaction was operated with ten times more Cu (7.3 mol% of Cu). As revealed by XRD analysis, the mean size of Cu crystallites on ZrO₂ is the smallest. Therefore, its excellent performance is probably connected with the nature of the support and with smaller size of metal NPs. It is worth to notice that Cu/C and Cu/ZnO, with supports of neutral and basic nature, exhibited also good activity, despite the large size of metal NPs, and low specific surface area of ZnO.

In the series of Ru catalysts, Ru/ZrO₂ and Ru/TiO₂ were the most active for 2-octanol dehydrogenation (Table 2), clearly pointing out the beneficial influence of amphoteric nature of support and small Ru particles (Table A.1). As for Cu catalysts, the selectivity to 2-octanone at 30% conversion was almost quantitative for all Ru catalysts. Then the selectivity decreased with increasing conversion, due to the formation

of C16 by-products (Fig. A.4). In contrary to Cu catalysts, no C24 by-products were observed. After 24 h, the selectivity to 2-octanone for Ru/ZrO₂ (S_{C8} = 71%, at X = 83%) was lower than for Ru/TiO₂ (S_{C8} = 96%, at X = 72%). In the literature, the dehydrogenation of 2-octanol has been reported only on Ru/AlO(OH) [4]. Full conversion was observed at 110 °C, using 45 times more Ru (4.5 mol%). The support effect has not been investigated until now for Ru catalysts in AAD reaction. As shown by the present results, the use of a carrier of an amphoteric nature generates the best results. It is worth to highlight, that under the same catalytic conditions, Ru catalysts perform similarly to Cu catalysts and Co catalysts [21], using a metal to alcohol ratio 10 times lower.

3.2.2. Activity towards primary alcohol and diol

For each metal, the two most active catalysts were tested in the dehydrogenation of 1-octanol and 1,2-octanediol (Table 3). Cu/ZrO₂ and Cu/C were active for 1-octanol dehydrogenation, giving 25% and 58% of conversion, respectively. However, the selectivity to octanal after 24 h was low, and C16 and C24 aldol condensation products were observed as the main reaction products. Ru/ZrO₂ was found not active in 1-octanol dehydrogenation, while Ru/TiO₂ was only moderately active. Even at low conversion (< 10%), the formation of C16 condensation products was already detected.

Cu/ZrO₂ and Cu/C were also active towards diol dehydrogenation, giving over 60% of conversion. Despite its significant activity for primary alcohol, Cu/ZrO₂ was highly selective to 1-hydroxy-2-octanone, preferentially dehydrogenating the secondary OH group. Traces of C16 and C24 condensation products were observed as by-products. In contrary, Cu/C was poorly selective to α-hydroxyketone and the main reaction products were C16 substances. It is worth noting that no product originating either from dehydrogenation of primary OH group or from further dehydrogenation was observed. Unfortunately, the activity of Cu/ZrO₂ dropped after recycling, and only 32% of conversion was reached after 24 h. However, the selectivity towards secondary OH group dehydrogenation was preserved. While comparing with other catalysts, Cu/ZrO₂ significantly prevails over Co/TiO₂ catalysts tested recently under the same reaction conditions [21]. Cu/C may find application in the synthesis of aldol condensation products [30,31], however it is beyond the scope of this study.

While tested in dehydrogenation of diol, Ru/ZrO₂ catalyst gave only 8% of conversion. Despite its good activity in secondary alcohol dehydrogenation, comparable to that of Cu and Co catalysts, the performance of Ru/ZrO₂ in primary alcohol or diol dehydrogenation was not competitive with that of other metals.

4. Conclusions

The support effect was studied for acceptor-less alcohol dehydrogenation with Cu and Ru catalysts, with 2-octanol as a model

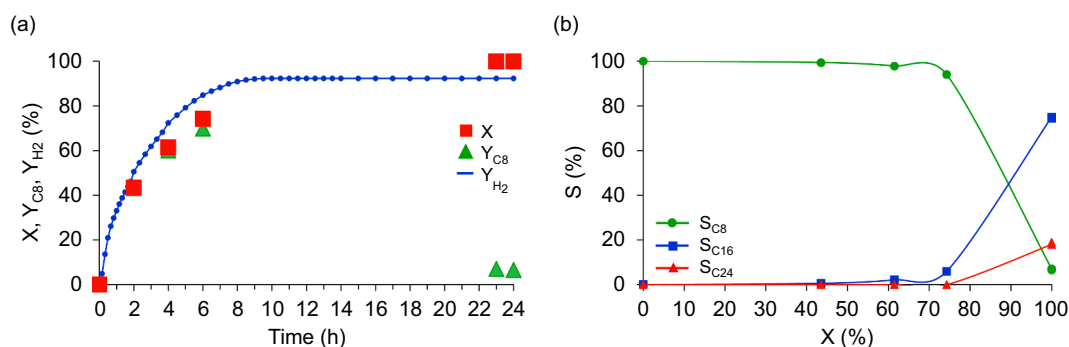


Fig. 1. Catalytic test results of 2-octanol dehydrogenation in the presence of Cu/ZrO₂: (a) conversion (X) and products yields (Y_{C8} and Y_{H₂}) vs time, (b) selectivity (S_{C8}, S_{C16} and S_{C24}) vs conversion (X).

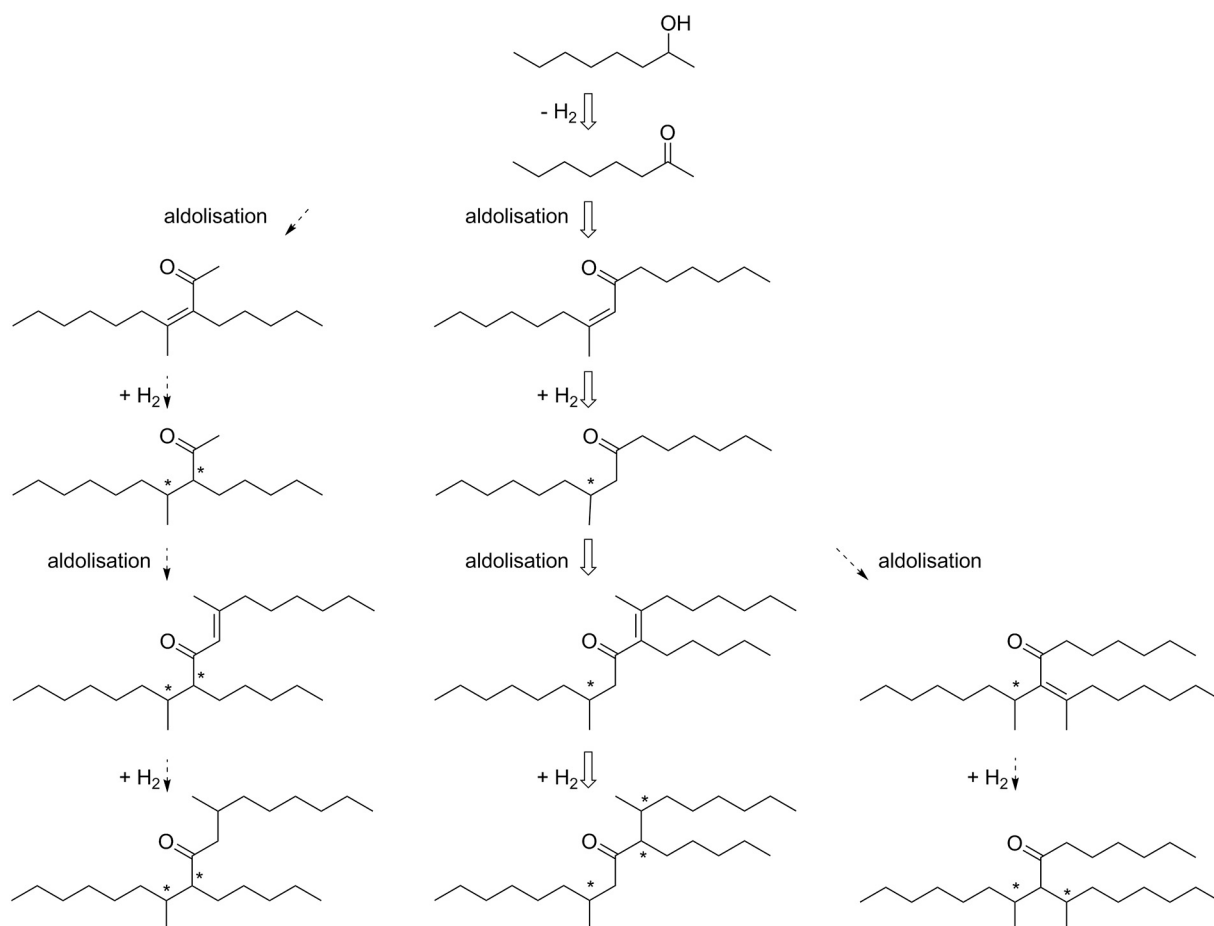


Fig. 2. Proposed reaction pathway associated with the dehydrogenation of 2-octanol to 2-octanone and subsequent reactions – aldol condensation/dehydration and hydrogenation. “ \Rightarrow ” refers to the main reaction pathway. “*” refers to chiral centres.

Table 3

1-octanol and 1,2-octanediol dehydrogenation in the presence of Cu and Ru catalysts. Reaction conditions: 0.5 g of catalyst for 1-octanol (0.8 mol% of Cu or 0.1 mol% of Ru); 1.0 g of catalyst for 1,2-octanediol (1.6 mol% of Cu and 0.2 mol% of Ru); 0.95 mol L⁻¹ alcohol, decane, 24 h, 145 °C, V_{total} = 45 mL.

Alcohol	Catalyst	X (%) ^a	S _{C8} (%) ^{a,b}	Y _{C8} (%) ^{a,b}
1-octanol	Cu/ZrO ₂	25	31	8
	Cu/C	58	5	3
1,2-octanediol	Cu/ZrO ₂	66	94	63
	Cu/ZrO ₂ – 2nd run	32	98	31
1-octanol	Cu/C	63	20	12
	Ru/TiO ₂	8	72	6
1,2-octanediol	Ru/ZrO ₂	2	72	2
	Ru/ZrO ₂	8	> 99.9	8

^a After 24 h.

^b In octanal (from 1-octanol) or 1-hydroxy-2-octanone (from 1,2-octanediol).

reaction. Catalysts supported on ZrO₂ exhibited the highest conversion, which must be connected with the amphoteric nature of the support and high dispersion of the metal. For both metals, the selectivity to 2-octanone was above 90% up to ca. 70% of conversion. At higher conversion, the selectivity decreased due to the formation of C16 and C24 compounds coming from aldol condensation/dehydration reactions, followed by hydrogenation.

The catalysts were also tested in dehydrogenation of 1-octanol and, for the first time, in reaction with 1,2-octanediol. Ru catalysts were hardly active. Among Cu catalysts, Cu/ZrO₂ exhibited promising results. Despite some activity in primary alcohol dehydrogenation, it gave good conversion (X = 66%) and selectivity (S_{C8} = 94%) towards the

dehydrogenation of secondary OH group in diol, with the formation of 1-hydroxy-2-octanone as the main reaction product. Cu/C also exhibited good activity in the dehydrogenation of diol (X = 63%), but the main reaction products were associated with aldol condensation.

Declaration of Competing Interest

There is no conflict of interest to declare.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.catcom.2020.106179>.

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