# Conversion of diols by dehydrogenation and dehydration reactions on bifunctional Cu-based oxides

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#### Introduction

Molecules containing multiple OH groups present potential applications as organic building blocks. Particularly, 1,3-butanediol (1,3-BDO) can be considered as a model molecule for the catalytic upgrade of polyols because it contains one primary and one secondary hydroxyl function. Thus, in this work we propose the gas-phase valorization of 1,3-BDO on Cu-Mg-Al mixed oxides that combine a metallic function (copper) with mild acid-base properties, and postulate a reaction pathway involving dehydrogenation and dehydration reactions (**Scheme 1**). The initial dehydrogenation of 1,3-BDO leads to aldol compounds (group HY) used in pharmaceutical and food formulations and as organic synthesis intermediates. Initial 1,3-BDO dehydration yields unsaturated alcohols (group UOL) which are used in polymer industry. Consecutive dehydration, hydrogenation or isomerization reactions yield saturated and unsaturated ketones (group K) and saturated alcohols (group SOL) which are important intermediates for the synthesis of solvents, pesticides, terpenoids, as well as steroids and anticancer drugs. The role of the size and amount of exposed Cu<sup>0</sup> particles on 1,3-BDO conversion was investigated. We also elucidated the participation of the catalyst surface acid-base or metal site in determining the initial dehydration or dehydrogenation pathway.



**Materials and Methods** Ternary Cu-Mg-Al mixed oxides containing 0.3-61.2 wt.% Cu were prepared by coprecipitation. Catalyst base site numbers  $(n_b)$  were measured by TPD of CO2. The dispersion of the Cu<sup>0</sup> particles (D) was measured by combining TPR and  $N_2O$ decomposition techniques. Catalytic tests were carried out after catalyst reduction (flowing H<sub>2</sub>, 573K) at 523K and

Scheme 1. Reaction pathways for 1,3-BDO conversion.

101.3 kPa in a fixed-bed reactor at contact times of 0.5-33.0 g cat h/mol of 1,3- BDO.

### **Results and Discussion**

The activity ( $r_{BDO}$ ) and the dehydrogenation/dehydration selectivity ratio ( $S_{.H2O}$ ) values obtained on ZCuMgAl catalysts are plotted in **Fig. 1** as a function of copper content (Z).



a function of Z.

On the ZCuMgAl catalysts  $r_{BDO}$  gradually increases with Z in a similar fashion as the exposed Cu<sup>0</sup> surface area ( $A_{Cu}$ ). Thus, the turnover rate values for these samples were similar, confirming participation of Cu<sup>0</sup> species in kinetically relevant reaction steps. The high  $S_{H2}/S_{H2O}$  ratio (**Fig. 1**), indicates that ZCuMgAl catalysts mainly promote the 1,3-BDO dehydrogenation route. The gradual increase of  $S_{H2}/S_{.H2O}$  with Z indicates that the catalyst dehydrogenating properties are enhanced at high loadings where the amount of exposed Cu<sup>0</sup> species is higher.

The distribution of dehydrogenation and dehydration products depends not only on the metal loading (**Fig.** 

2) but also on the oxide base properties that decrease with Z. Fig. 2A suggests that low copper loading ZCuMgAl oxides do not promote formation of HY compounds because abundant surface base sites on these samples completely transform them in compounds of groups RA and K. However, the contribution of group HY increases with Z because of the large Cu<sup>0</sup> particles and low number of base sites on high Cu-content ZCuMgAl catalysts. These results are in line with a previous work showing that on catalysts with large Cu<sup>0</sup> particles, the HYK-Cu<sup>0</sup> site interaction is weak and the HYK molecule is released to the gas phase before being

converted in consecutive reactions [1] (Scheme 1). The distribution of dehydration products on ZCuMgAl catalysts (Fig. 2B) shows that UOL is favored at low Z values. At higher Z values, the consecutive hydrogenation of the C=C bond of UOL toward SOL occurs as a consequence of the increasing  $A_{Cu}$  and the resulting hydrogenating-dehydrogenating properties.



Figure 2: Product distribution on ZCuMgAl vs. Z.

### Significance

Bifunctional Cu-Mg-Al catalysts efficiently promote the upgrading of 1,3-butanediol by dehydrogenation and dehydration reactions toward valuable oxygenates without supply of costly  $H_2$ . In particular, Cu-Mg-Al mixed oxides with high copper content are the most promising materials because of their high activity (attributed to their large number of surface  $Cu^0$  sites) and high selectivity toward valuable multifunctional oxygenates such as the hydroxyketone.

## References

1. P.A. Torresi, V.K. Díez, P.J. Luggren, J.I. Di Cosimo, App. Catal. A: General, 2013, 458, 119-129.