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 aldehyde compounds (group HY) used in pharmaceutical and food formulations and as organic synthesis intermediates. Initial 1,3-BDO dehydroxylation yields unsaturated alcohols (group UOL) which are used in polymer industry. Consecutive dehydration, dehydrogenation 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 size of the scale and amount of exposed Cu 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 dehydroxylation or dehydroxylation pathway.

Materials and Methods

Ternary Cu-Mg-Al mixed oxides containing 0.3-61.2 wt.% Cu were prepared by co-precipitation. Catalyst base site numbers (nB) were measured by TPD of CO2. The dispersion of the Cu particles (D) was measured by combining TPR and N2O decomposition techniques. Catalytic tests were carried out after catalyst reduction (flowing H2, 573K) at 523K and 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 (rBDO) and the dehydrogenation/dehydration selectivity ratio (SHY/SUOL) values obtained on ZCuMgAl catalysts are plotted in Fig. 1 as a function of copper content (Z).

Figure 1. rBDO and SHY/SUOL (at 30% conversion) on ZCuMgAl as a function of Z.

On the ZCuMgAl catalysts rBDO gradually increases with Z in a similar fashion as the exposed Cu3+ surface area (Aυ). Thus, the turnover rate values for these samples were similar, confirming participation of Cu3+ species in kinetically relevant reaction steps. The high SHY/SUOL ratio (Fig. 1), indicates that ZCuMgAl catalysts mainly promote the 1,3-BDO dehydroxylation route. The gradual increase of SHY/SUOL with Z indicates that the catalyst dehydroxylation properties are enhanced at high loadings where the amount of exposed Cu3+ species is higher.

The distribution of dehydroxylation 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 Cu3+ particles on 1,3-BDO surface sites is weak and the HYK-Cu3+ 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 dehydroxylation products on ZCuMgAl catalysts (Fig. 2B) shows that UOL is favored at low Z values. At higher Z values, the consecutive dehydroxylation of the C=C bond of UOL toward SOL occurs as a consequence of the increasing Aυ and the resulting dehydroxylation-methanol properties.

Significance

Bifunctional Cu-Mg-Al catalysts efficiently promote the upgrading of 1,3-butanediol by dehydroxylation and dehydration reactions toward valuable oxygenates without supply of costly H2. 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 Cu3+ sites) and high selectivity toward valuable multifunctional oxygenates such as the hydroxyketone.

References