Recyclable Cu-Fe Catalysts Derived from Cu-Fe Layered Double Hydroxides for Acceptorless Dehydrogenation of Alcohols

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Abstract: The development of an active and robust catalyst for acceptorless dehydrogenation (AD) of various alcohols is highly desired. We herein prepared Cu-Fe catalysts from a Cu-Fe layered double hydroxide (LDH) precursor by H_2 treatment as a green reduction process. These Cu-Fe catalysts were catalytically active towards various secondary alcohols with a high yield (>92%) of the corresponding ketone product and reusable after its reactivation with H_2 treatment with no significant loss of activity.

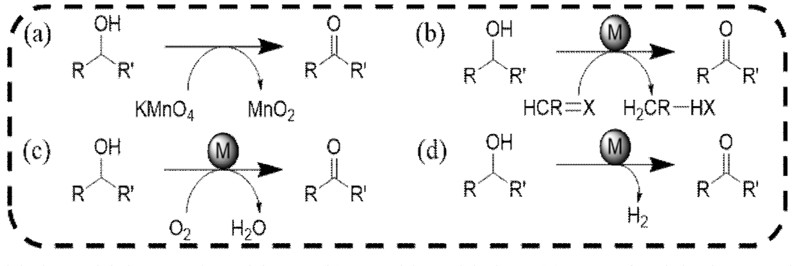
Keywords: AD of alcohols, Cu-Fe catalysts, Cu-Fe LDHs.

1. Introduction

The oxidation of alcohol to form carbonyl compounds, such as ketones or aldehydes, is one of the most important transformations in organic reactions.[1] To date, this type of transformation has been mainly developed with several pathways: a) traditional oxidation with inorganic oxidants, b) aerobic oxidation, c) transfer dehydrogenation, and d) acceptorless dehydrogenation (Scheme 1). The catalytic AD reaction of alcohol is considered a green and atom-efficient synthetic approach for the direct production of carbonyl compounds without sacrificial H_2-acceptor compounds. Instead, molecular H_2 is liberated and could be implemented in a "hydrogen economy".[2]

There are several reports on heterogeneous catalysts for the AD of alcohols, but they are susceptible to air exposure. For example, K. I. Shimizu and co-workers reported that a Co/TiO_2 catalyst was air sensitive in the AD reaction of cyclododecanol.[3] They stated that the Co/TiO_2 catalyst was significantly deactivated after exposure to air for 0.5 h. Recently, Y. Zhu et al. developed highly efficient and recyclable $Cu(0)/Cr_2O_3$ catalysts prepared from an LDH precursor for the AD reaction with numerous alcohol substrates.[4] However, the $Cu(0)/Cr_2O_3$ catalysts are not environmentally acceptable due to the presence of toxic chromium species. Therefore, the development of robust and environmentally friendly catalysts is essential for the AD reaction.

In the present report, we developed an environmentally acceptable Cu-Fe catalyst from Cu-Fe LDH precursors. The Cu-Fe catalyst was prepared by reducing the Cu-Fe LDH precursor with H_2 treatment prior to the AD reaction. The used catalyst was easily separated from the solution reaction with an external magnet due to its magnetic properties.



Scheme 1. (a) Oxidation with inorganic oxidants; (b) Aerobic oxidation; (c) Transfer dehydrogenation and (d) Acceptorless dehydrogenation.

2. Experimental

The Cu-Fe LDH precursor was prepared using simple co-precipitation of $Cu(NO_3)_2{\cdot}3H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ with NaOH as a precipitator and water as a green solvent. The mixture solution was refluxed under air atmosphere at 333 K for 24 h. The Cu-Fe LDHs were subsequently calcined under a reductive atmosphere (H_2 gas) at 573 K to produce fresh Cu-Fe catalysts.

3. Results and discussion

The XRD pattern of Cu-Fe(3)LDH shows a series of (00l) peaks at regular intervals corresponding to the stacking periodicity of a layered structure (Figure 1(a)). The typical (003), (006), (012), and (015) reflections of Cu-Fe(3)LDH show the rhombohedral structure with the lattice parameters of a = 3.19 Å and c = 20.81 Å using hexagonal indices. The characteristic reflections corresponding to the LDH phase disappeared with the concomitant formation of new reflections comprising Cu metal species and Fe_3O_4 species after H_2 treatments at 573 K. The peak pattern of the Cu-Fe(3)HT-573 catalyst was observed at $2\theta = 43.3°$, 50.5°, and 74° assigned to the Cu peaks (JCPDS 04–0836) and peaks at $2\theta = 35.4°$ and 62.4° attributed to Fe_3O_4 (JCPDS 75-0033). Such a topotactic transformation of the Cu-Fe(3)LDH after H_2 treatment is illustrated in Figure 1(b), based on the XRD result.

The scope of the Cu-Fe(3)HT-catalysed AD of alcohols is shown in Table 1. Through catalytic AD, aromatic (entry 1), cyclic (entry 2), and aliphatic secondary alcohols (entry 4) were converted to the corresponding ketone with an outstanding yield (>92%) using Cu-Fe(3)HT catalysts. The Cu-Fe catalyst was, however, rather inactive towards primary alcohols, e.g., benzyl alcohol, since the yield of benzaldehyde was 31% (entry 4). Notably, the addition of the base compound and an increase in reaction temperature did not enhance the catalytic performance of Cu-Fe(3)HT catalysts towards the AD of benzyl alcohol. We also found that Cu-Fe(3)_HT is resistant to air exposure, and it was steadily reusable after being retreated with H_2 for the AD of 1-phenylethanol (Table 1, entry 1).

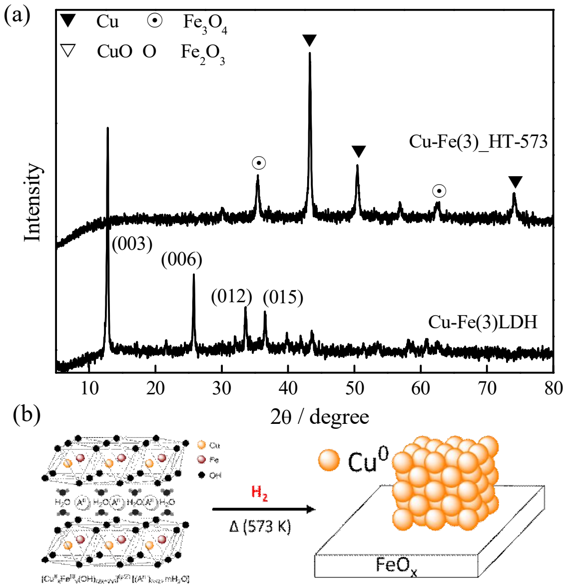
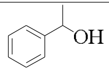
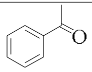
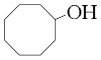
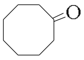
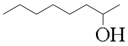
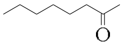
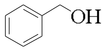
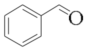


Table 1 AD of various alcohols using Cu-Fe(3)_HT catalysts

Entry	Substrate	Product	Conv (%)	Yield (%)
1			100; 96^a; 55^b;94^c 100^d	97; 82^a; 55^b; 88^c 86^d
2			92	92
3			92	92
4			34	31

Reaction conditions: Cu-Fe(3)HT catalyst, 0.1 g; substrate, 1.1 mmol; p-xylene, 3 mL; decalin, 0.07 g; 388 K; 20 h; N_2 1 atm. [a]2nd run. [b]3rd run. [c]4th run after reactivated by H_2 treatment at 573 K. [d]1st run after exposed by air for 24 h at r.t.

Figure 1 (a) XRD patterns of Cu-Fe(3)LDH and Cu-Fe(3)HT-573, (b) schematic illustration of topotactic transformation of Cu-Fe(3)LDH after H_2 treatment

4. Conclusions

In summary, a Cu-Fe(3)LDH precursor was successfully synthesized with a simple co-precipitation method under mild conditions. The topotactic transformation of the Cu-Fe(3)LDH proceeded by H_2 treatment to the Cu metal-metal Fe oxide composite (Cu-Fe(3)HT catalysts) was also confirmed. The Cu-Fe(3)HT catalyst was found to be reusable, stable and highly active towards a catalytic AD of various secondary alcohols.

References

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