Ce doped $LaCoO_3$ perovskite for liquid-phase selective oxidation of benzyl alcohol using molecular oxygen as oxidant

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Introduction

Selective oxidation of alcohols to the corresponding aldehydes and ketones is one of the most important functional transformations in organic synthesis owing to the large demand in perfumery and food industries. In case of benzaldehyde, it was initially proposed to be synthesized by hydrolysis of benzalchloride derived from toluene chlorination, and even at today, benzaldehyde is still commercially produced by this way in many factories. However, this route releases a large amount of contaminants, e.g., the unused organic chlorine, the by-product benzoic acid, which are harmful to the environment. With the legislation on the emission of contaminant and from the viewpoint of environmental protection, the development of an eco-friendly way using air or molecular oxygen as oxidant is more preferred.[1,2] However, the search for catalyst that can activate molecular oxygen and catalyze it reacting with benzyl alcohol to yield benzaldehyde with considerable efficiency is still on the way.[3]

Perovskite-type oxides with ABO_3 structure have attracted great interest in catalysis because of their unique structural features and thermal or hydrothermal stability.[4,5] The A- and/or B-site of ABO_3 can be substituted by many foreign metal cations without destroying the matrix structure, as long as the tolerance factor is in the range of 0.7–1.1.[5] Thus the oxidation state of B-site cations and/or the amount of oxygen vacancy can be controlled, optimizing the material for special use.

In this work, we prepared a series of Sr and Ce-doped $LaCoO_3$ perovskite catalysts for the selective oxidation of benzyl alcohol to benzaldehyde with molecular oxygen. Results shown that such catalysts can exhibit up to 90% benzyl alcohol conversion within 6 hours, which is comparable to that of supported gold catalysts,[6] indicating that perovskite oxides are promising catalyst for this reaction. This is the first work reporting the use of perovskite oxides ($LaCoO_3$) as catalyst for this type of reaction to the best of our knowledge

Materials and Methods

The catalyst was synthesized by sol-gel method using ethylene glycol as complex. After calcination at 600 ˚C for 5 h, the perovskite structure was formed. Catalytic tests were carried out in a three-necked round-bottomed bottle (50 mL) filled with 0.2 g catalyst, 20 mL of toluene, 20 μL benzyl alcohol and 20 μL dodecane, which was heated in an oil bath. A water-cooling condenser (10 ˚C) was fixed to the reactor to avoid the evaporation of reactants and/or product. The oxygen was bubbled at a flow rate of 50 mL/min. The rotating speed was controlled at 500 rpm and the temperature was kept at 90 ˚C. The sample was extracted at desired reaction time and analyzed by an Agilent 7890 GC equipped with a HP-5ms column and flame ionization detector (FID). The conversion for benzyl alcohol was calculated using dodecane as internal standard.

Results and Discussion

Figure 1 (A) shows the activity of $La_{0.9}Sr_{0.1}CoO_3$, $LaCoO_3$ and $La_{0.9}Ce_{0.1}CoO_3$ for benzyl alcohol oxidation using oxygen as oxidant at reaction time of 6 h, which indicated that the $La_{0.9}Ce_{0.1}CoO_3$ sample is more favorable for the reaction. By considering the changes in the oxidation state of Sr^{2+}, La^{3+} and Ce^{4+}, it seems that the substitution of metal ions with high oxidation state is more preferred in designing the catalyst, which could be in part due to the influence of the oxygen vacancy from the viewpoint of electroneutrality. The intrinsic influences by such substitutions on the physicochemical properties of samples and that the relationship between the physicochemical properties and the activity is still under investigation. **Figure 1** (B) shows the conversion of benzyl alcohol as a function of reaction time over the $La_{0.9}Ce_{0.1}CoO_3$. As expected the conversion increases with the increase of reaction time, while considerable activity (*ca.* 55%) still can be achieved even at 2 h. This indicates that perovskite oxides can be promising substitutes of noble metal catalysts applied for selective oxidation of alcohols using oxygen as oxidant.

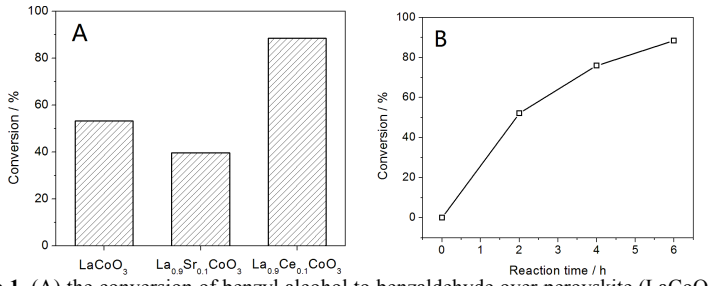

Figure 1. (A) the conversion of benzyl alcohol to benzaldehyde over perovskite ($LaCoO_3$) and doped perovskite ($La_{0.9}Sr_{0.1}CoO_3$ and $La_{0.9}Ce_{0.1}CoO_3$); (B) the conversion varied with the reaction time over $La_{0.9}Ce_{0.1}CoO_3$.

Significance

Ce doped perovskite ($La_{0.9}Ce_{0.1}CoO_3$) showed excellent activity for selective oxidation of benzyl alcohol to benzaldehyde using oxygen as oxidant, which is comparable to that of noble metal catalysts reported in literature. To the best of our knowledge this is the first time using perovskite oxides as catalysts for such reactions, opening a new vista for designing cheap and efficient catalyst for industrial use in future.

References

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