

NEW CoSn/ZnO CATALYSTS IN THE REDUCTION OF METHYL OLEATE INTO UNSATURATED ALCOHOLS

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Introduction

The hydrogenolysis of fatty methyl esters issued from agricultural compounds is an attractive way to prepare the fatty alcohols and particularly unsaturated fatty alcohols. In fact, unsaturated compounds, such as oleyl alcohol (methyl cis-9-octadecen-1-ol: liquid at room temperature), are important materials for the manufacture of heavy-duty liquid detergents, cosmetics, pharmaceuticals, toiletries, antifoaming agents, etc [1-3]. In industrially available processes, hydrogenation is carried out at high temperature and high pressure (200–300°C and 20–30 MPa), usually using copper or zinc chromium catalysts. In our laboratory, it was demonstrated that bimetallic systems such CoSn supported over zinc oxide [4] favor the reduction of methyl oleate into oleyl alcohol in less severe conditions (270°C and hydrogen pressure of 8 MPa). The active center was a mixed species where a cobalt atom was close to two tin atoms. It was also shown that CoSn supported over zinc oxide catalyst was more selective than CoSn supported over alumina solid [5, 6]. Nevertheless, two sides reaction modified the selectivity of the desired unsaturated alcohol (oleyl alcohol) :

1. The transesterification reaction between the alcohol formed and methyl oleate producing heavy esters (ex : oleyl oleate).
2. The cis/trans isomerization of the methyl oleate (cis) into methyl elaidate (trans).

These bimetallic systems are interesting but they are less active in the reduction of methyl oleate into unsaturated alcohols than the bimetallic RuSn solid [7-9]. Even the most active CoSn/ZnO [4] catalyst prepared with chloride salts is still less competitive than the RuSn catalysts. Consequently, in order to improve the catalytic properties of such solids in the hydrogenation of methyl oleate into oleyl alcohol, the nature of the metallic precursor salts used during the preparation of the catalysts was studied.

Materials and Methods

All the catalysts were prepared with a bulk cobalt loading around 3 wt% and a bulk (Sn/Co) molar ratio of 1. The catalysts were prepared by co-impregnation with different cobalt and tin salts chloride salts (Chloride, nitrate, tartrate and acetate). Before use and characterizations, all catalysts prepared by co-impregnation were reduced with hydrogen at 300°C and passivated with air at room temperature. When $\text{Co}_2(\text{CO})_8$ was used as cobalt precursor, the solid formed was kept under inert atmosphere in order to avoid any air oxidation. This catalyst was used without further reduction step. All the solids were characterized with XPS, XRD, TRP, TEM, BET analysis.

The methyl oleate hydrogenation was carried out in an autoclave under 270°C and 8MPa of hydrogen. The products were analyzed by gas chromatography.

Results and Discussion

The CoSn/ZnO catalysts prepared with cobalt carbonyl or cobalt chloride are more actives than the ones prepared from nitrate or tartrate precursors in the reduction of methyl oleate into unsaturated alcohols. All catalysts lead to the formation of heavy esters at low conversion (20%) with around 80% of selectivity while, at high conversion (80%), the unsaturated alcohols are formed (between 40 and 60% of selectivity). The different characterizations lead to a more concise definition of the catalyst due to a better knowledge of catalyst surface. The selectivity is governed by the reduction of the heavy esters formed, which can occur in the presence of small metallic Co-Sn particles, well dispersed on the catalyst surface and a contribution of the support to the adsorption of hydrogen. In fact, the catalyst contains a mixed of metallic cobalt and tin species, CoSn_2 (active centers of the reaction) leading to an increase of activity and selectivity. In order to obtain well dispersed species, the carbonyl cobalt precursor seems to be the best salt for the hydrogenation of methyl oleate since the selectivity to unsaturated and saturated alcohols of 70% at 80% of conversion was observed. On the other hand, In the presence of chloride or nitrate salt, the CoSn particle size was bigger leading to a decrease of catalytic properties. Our findings provide some insight of the mechanism of the hydrogenation of methyl oleate into unsaturated alcohol. In fact, the transesterification reaction firstly occurs since the alcohol desorption rate is lower than the transesterification reaction rate. Secondly, the reduction of the heavy esters into unsaturated alcohols and the hydrogenation of methyl oleate into alcohols are completed. This second step occurs only if the particles are well dispersed, small and in an adequate content on the surface to allow the reduction of the heavy esters.

Significance

The preparation of a new CoSn catalyst from carbonyl precursor leads to a very active and selective catalyst in the free solvent synthesis process of unsaturated alcohols from fatty methyl esters.

References

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