Research Progress in Catalysts for Fatty Acid Ester Hydrogenation

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Abstract. Fatty alcohols and its derivatives have wide applications in industrial production and constitute one of the largest kind within the oleo-chemicals, and could be got by heterogeneous catalytic hydrogenation of fatty acids esters over suitable catalysts. The new progress in the efficiency supported copper, palladium, ruthenium catalysts and metal hydrides for fatty acid ester hydrogenation was reviewed, further development was also discussed.

1. Introduction

Fatty alcohols are a kind of amphiphilic molecules formed by one or more hydroxyl groups linked with an aliphatic chain and find application in emollients, emulsifiers, thickeners in cosmetics and food industries. The chain of fatty alcohols normally has 6 to 22 carbon atoms. Natural fatty alcohols are gained from renewable origins like oils, fats and waxes of vegetable or animal resource. While synthetic fatty alcohols are get from petrochemical materials like paraffins or olefins. Fatty alcohols constitute one of the largest kinds of the oleochemicals. To ensure a high level of product safety to the environment and users, renewable resources are more inclined to petrochemical raw materials, and therefore are considered as ideal feedstocks for fatty alcohols production.

Fatty alcohols from mass production by hydrogenation of fatty acid esters, which is a technological process that has not changed very much for decades. Industrial hydrogenation of fatty acid esters to fatty alcohols has been conducted over a Cu/Cr catalyst under mild condition with high hydrogen pressures from 25 MPa to 30 MPa and reaction temperature within the range of 200 ℃ to 300 ℃. However, the poisonous nature of Cr in the catalyst unable it suitable for extensive use. Therefore, the development of a highly active catalytic system with good stability is a research hotspot in this field.

In recent decades, a series of explorations and experiments have been carried out to improve the hydrogenation catalyst and optimize the hydrogenation process conditions, which have been well explained in the previous literature[1,2]. The research of fatty acid ester hydrogenation has been developed rapidly in recent years, the milestone achievements and the latest work of the catalytic reaction in the fixed-bed, semibatch or batch reactor are introduced in this paper.
2. Catalysts for fatty acid ester hydrogenation to fatty alcohol

2.1. Copper catalysts
Cu-Zn catalyst was prepared and used for the hydrogenation of fatty acid methyl esters at subcritical conditions. The conversion of fatty acid methyl ester achieved 99.5% and the selectivity of fatty alcohol achieved 99.6%, when the reaction was conducted under temperature of 250 °C, pressure of 6.0 MPa, volume ratio of hexane to fatty acid methyl ester 7:1, space velocity of 0.8 h⁻¹, and volume ratio of hydrogen to oil 250:1. The result indicated that Cu-Zn catalyst was surpass Cu-Cr catalyst[3].

CuO/ZnO/Al₂O₃ catalysts were synthesis by change the initial concentration of alkali in the co-precipitation method. The catalyst originated from layered double hydroxides structure showed the highest activity in the fatty esters hydrogenation as well as high selectivity to fatty alcohol, producing fatty alcohol with a yield of more than 98%. The high catalytic behavior was owe to relatively high dispersion and the high reducibility of copper species. The Cu⁺/Cu⁰ were supposed to be the active site for the hydrogenation[4].

Bimetallic and monometallic catalysts including Cu and/or Fe species were synthesis by a co-precipitation process and selective hydrogenation of ethyl stearate to stearyl alcohol was used for catalytic behavior testing. The results indicated that the bimetallic catalyst was observed to be even more active compared to the monometallic catalyst. A selectivity to alcohol reached to above 99% at a conversion of 97% in the hydrogenation reaction over Cu/Fe bimetallic catalyst. Those could be explained by the fact that synergistic effect of Fe and Cu species arose and led the enhancement of the catalytic activity[5].

The Cu-Al-Ba catalyst was gained by co-precipitation method and was used in the methyl stearate hydrogenation. The catalyst preparation condition was optimized and counterflow coprecipitation was used followed by treatment with organic solvent. At the optimal condition, the conversion of methyl stearate was 98% and the selectivity of stearyl alcohol was 96.6%[6].

Novel highly efficient chromium free Cu-Zn-Al-Ba catalyst was gain by changing dropping sequence in the procedure of co-precipitation. The catalytic activity and reusability of the catalyst was measured by the hydrogenation of C₁₂ - C₁₈ fatty acid methyl esters for fatty alcohols preparation. The results showed that the chromium free Cu-Zn-Al-Ba catalyst prepared by adding mixed salt solution to precipitation agent had good catalytic behavior in the hydrogenation. The yields and selectivities could to be above 90%[7]. When the Cu-Zn-Al-Ba catalyst was used in the catalytic hydrogenation of methyl stearate to stearyl alcohol with n-hexane as the solvent, the conversion of methyl stearate and the yield of stearic alcohol reached more than 96% and about 95%, respectively, at the ideal hydrogenation reaction condition[8].

2.2. Ruthenium catalysts
Monometallic Ru-B and Sn catalyst supported on Al₂O₃ was synthesis by impregnation of ruthenium salt or tin salt solution. The solution containing Ru or Sn precursors was added to the carrier, and the slurry was stirred slowly for 1 h at room temperature, and then reduced with excess aqueous sodium borohydride solution. The metal activity of Ru was greatly reduced by Sn addition. The existence of support changed the particle size of Ru and the interaction between Ru and Sn, which strongly affected the activity and selectivity of the catalyst[9].

The Ru-B/Al₂O₃ catalyst was synthesis by the incipient wetness process. The support was wetted with accurately the pore volume of an aqueous solution of metal precursor salts in the required quantity to get the desired metal content. The wet samples were kept still for 12 h. A procedure of reduction with excess aqueous sodium borohydride solution was then conducted. The catalyst was then prepared after reduction, cooling, and hydrogen purging with N₂. The results showed that Ge is deposited on both the meal function aggregates and on the support surface. The metallic activity of Ru was significantly modified. Optimum ratio of Ge to Ru for oleyl alcohol production was got[10].
2.3. Palladium catalysts

Diatomite supported Pd-Cu bimetal nanocatalyst were prepared by co-impregnation method. It was showed that the nanoparticles of metal were evenly distributed on the support, and their dimension was centred around 8 nm with a relatively narrow size distribution. The catalyst was used for hydrogenation of long-chain aliphatic esters, including methyl laurate, methyl palmitate, and methyl stearate. The result displayed that Pd-Cu/diatomite catalyst showed good performance for the selective hydrogenation via the synergistic effect between the particles of metal and the diatomite support, giving a 1-hexadecanol yield of 82.9% at the substrate conversion of 98.8%[11].

Polyethylene glycol monomethyl ethers with different molecular weights were used. Thermoregulated ionic liquid were prepared and used as the stabilizer to establish the termoregulated phase-separation catalytic system containing the Pd nanoparticles catalyst. The Pd nanoparticles exhibited high stability in the present of termoregulated ionic liquid, and endowed the catalytic system with a good termoregulated phase separation property, the monohasic reaction combined with a biphasic separation. The functional quaternary ammonium salt cation and nonionic polyethylene glycol chain of the prepared ionic liquid acted as anchors to stabilize the Pd nanoparticles, which enabled the nanoparticles catalytic system with a high dispersion and stability. PdNPs/ILMPEG illustrated an excellent catalytic behavior for the hydrogenation of fatty acid methyl ester, the conversion of carbonyl group could be reached up to 97%[12].

2.4. Metal hydrides

A new route for synthesis of fatty alcohol by hydrogen and hydride transfer reduction was proposed. Lauryl alcohol was prepared from methyl laurate by transfer reduction of hydrogen and hydride in liquid phase via non-catalytic reactions. Pure or alumina-supported metal hydride (NaBH₄) and methanol were used as H⁻ donor and H⁺ donor, respectively. Typical reduction reactions were conducted at 323 K and atmospheric pressure in a semibatch reactor. 100% fatty alcohol selectivities were achieved. Fatty acid methyl esters with shorter carbon chain length and without unsaturation were easily hydrogenated using NaBH₄/Al₂O₃ and methanol, getting high conversions and fatty alcohol selectivities[13].

2.5. Conditions of fatty acid ester hydrogenation to fatty alcohol

The name of catalysts, fatty acid esters, hydrogenation pressure, reaction time, reaction temperature, solvent, conversion, yield, reactor, LHSV and the ration of H₂ to oil in hydrogenation experiments were summarized in Table 1. It could be seen from Table 1 that the hydrogenation pressure was raged from atomosphere to 6.0 MPa, and the hydrogenation temperature and time ware in the range of 50 to 290 ℃ and 2 to 7 h, respectively. Tetrahydrofuran, n-dodecane, n-hexane, n-heptane, toluene were used as solvent in the hydrogenation. The conversion and yield reached up to >96% and >93%, respectively, in the batch, semibatch or fixed-bed reactor.

3. Conclusions

In the past few decades, researchers have successfully developed a series of highly efficient hydrogenation catalysts for hydrogenation of fatty acid esters to fatty alcohols. Improvements in the performance behavior of the hydrogenation catalyst were based on the recognition of the importance of reactant-support, metal-support and metal-metal synergy. It is believed that further development of a molecular understanding of catalysis will lay a foundation for the rational design of new and improved catalysts or routes for fatty acid ester hydrogenation.

| Catalyst     | Ester    | P    | T  | t    | Solvent | Ref. | Con. | Yield | Reactor          | LHSV | H₂/oil |
|--------------|----------|------|----|-----|---------|------|------|-------|------------------|------|--------|
| Cu-Zn        | FAME     | 6.0  | 250 | ℃ / | hexane  | [3]  | 99.5%| 99.6% | Fixed-bed       | 0.8  | h⁻¹ 250:1 |
| CuO/ZnO/Al₂O₃| Ethyl Stearate | 3.0  | 230 | ℃/h | hexane  | [4]  | 96% | >98%  | batch            | /    | /      |
| Catalyst          | Precursor             | Pressure | Temperature | Solvent     | Duration | Conversion | Selectivity | Method   |
|-------------------|-----------------------|----------|-------------|-------------|-----------|------------|-------------|----------|
| Cu/Fe             | Ethyl stearate        | 3.0 MPa  | 230 °C      | 4h hexane   | [5]       | 97%        | >99%        | batch    |
| Cu-Al-Ba          | Methyl stearate       | 6.0 MPa  | 240 °C      | 5h          | /         | 98%        | 96.6%       | batch    |
| Cu-Zn-Al-Ba       | Methyl stearate       | 3.0 MPa  | 230 °C      | 4h n-hexane | [7,8]     | 96%        | 95%         | batch    |
| Ru-Sn-B/Al₂O₃     | Methyl oleate         | 5.0 MPa  | 290 °C 6h   | n-dodecane  | [9]       | ~100% ~100%| batch       | /        |
| Ru-B/Al₂O₃        | Methyl oleate         | 5.0 MPa  | 290 °C 2h   | n-dodecane  | [10]      | 99.46%     | 98.0%       | batch    |
| Pd-Cu/diatomite   | Methyl palmitate      | 5.5 MPa  | 270 °C 7h   | n-heptane   | [11]      | 98.8%      | 82.9%       | batch    |
| PdNPs/ILMPEG      | FAME                  | 6.0 MPa  | 210 °C 4h n-heptane, toluene | [12] | 97.1% | / | batch |
| NaBH₄/Al₂O₃       | FAME                  |          |             | Atmosphere  | tetrahydrofuran | [13] | 100% | 93% | semibatch |

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