Application Progress of Ester Hydrogenation Catalysts

Yifei Li*

College of Chemical Engineering, East China University of Science and Technology, Shanghai, China

*Corresponding author: 20000417@mail.ecust.edu.cn

Abstract. Ester hydrogenation is a fresh approach to preparing alcohols or monoesters, which is used to obtain the required specific length of carbon atoms to replace the alcohol molecules to produce the corresponding esters or alcohols by the action of a catalyst, and has various applications in energy, chemical and food industries. The process involves the hydrogenation of the reactant esters to produce alcohols through catalysis. The process has the advantages of mild reaction conditions, few by-products and simple operation. Currently, there are two main approaches to ester-catalyzed hydrogenation: one is the application of noble metal hydrogenation catalysts, which is generally carried out in the air; the other is loaded metal catalysts that control the reaction activity by adjusting the reaction temperature, metal particle size and other factors. This paper reviews and summarizes the current status and problems in the application of these three methods: platinum-based non-homogeneous catalytic hydrogenation, transition metal-loaded catalysts and the application of rare earth metals.

Keywords: Ester catalytic hydrogenation, catalyst, platinum-based catalytic hydrogenation, transition metal-loaded catalyst, rare earth metal applications.

1. Introduction

Organic reactions with decreased oxidation number of carbon atoms are called reduction reactions, which manifest themselves as a decrease in O atoms and increase in H atoms [1]. The reduction of esters is manifested as the conversion to alcohols by the involvement of carbonyl-containing compounds in the reaction.

Esters are structurally similar to carboxylic acids and therefore have some properties similar to carboxylic acids, such as the nucleophilic reactivity of the carbonyl group. However, due to the lone pair of electron conjugation of the alkoxy-terminated oxygen, the C-O bond in the ester has some double bonding properties that will give electron conjugation to the carbonyl group, and thus the carbonyl carbon reactivity is weaker than that of aldehydes and ketones and acyl halides, and the reduction activity is reduced. Because of the low nucleophilic reactivity of the carbonyl bond in esters, the hydrogenation of carboxylic acid esters to alcohols is more difficult to carry out than the hydrogenation of aldehydes and ketones, and it requires higher temperatures and more suitable catalysts to carry out.

The commonly used chemical-reducing agents are metal hydrides and sodium metal under inert organic solvents. The reduction activity of the commonly used metal hydrides for esters is: $LiAlH_4$ > $LiBH_4$ > $NaBH_4$. For ester reduction reactions, metal borohydride is less active than lithium aluminum hydride. When the reducing agent is Na-based, it can be used to prepare unsaturated alcohols regardless of the single or double-molecule reduction, as the carbon-carbon double bond in the molecule can be left unaffected. In sodium-alcohol systems (polar solvents), a radical negative ion intermediate gives primary alcohol, which is names as the Bouveault-Blanc reduction reaction [2]; bimolecular reduction of fatty acid esters in sodium-ether or toluene and xylene systems (non-polar solvents) gives α-hydroxy ketones (dehydrin), named as the ketohydrin condensation [1,2].

The above-mentioned reductants have some intrinsic disadvantages including high price and low reactivity. For example, lithium aluminum hydride as a reducing agent is less selective and prone to the simultaneous reduction of other functional groups of the substrate and is only of good use in the laboratory. For large-scale reactions, catalytic hydrogenation is a more ideal approach. Hydrogenation under the action of copper-chromium oxides with strong reaction conditions yields two-molecule alcohols, and the lactone can be obtained as a diol without affecting the phenyl group [1]. Since conventional chromium-containing catalysts can pollute the environment and hydrogenation needs high temperatures (250-300 °C) and high pressures (25-35 MPa), broad-spectrum hydrogenation catalysts using precious metals such as Ru, Pd and Pt are more commonly used in widespread applications [3]. These are more active but also more costly and have limited applications when reactant dosage is large or reaction conditions are too harsh [4-8]. Therefore, today's research is directed towards both higher catalytic reactivity, lower costs, higher efficiency and environmentally friendly characterization.

2. Platinum-Based Non-Homogeneous Catalytic Hydrogenation.

Platinum (Pt) is the most commonly used precious metal catalyst and is by far the most widely used catalyst in industry, but it is also relatively expensive. There are four common central metals for platinum-based catalysts: platinum, ruthenium, rhodium and palladium, of which platinum (Pt) and rhodium (Rh) are less toxic and therefore more commonly used. However, for the hydrogenation of esters, platinum-based catalysts do not necessarily have optimal performance, so the reaction will be optimized from three perspectives: multiphase reaction, central metal and reactant activation.

2.1. Non-Homogeneous Catalytic Hydrogenation

The non-homogeneous catalytic hydrogenation reaction is characterized by a multi-phase catalytic reaction and consists of five stages: (i) Reactant molecules diffuse onto the catalyst surface; (ii) Reactant molecules are adsorbed onto the catalyst surface; (iii) Chemical reaction of adsorbed reactants takes places to form adsorbed product molecules; (iv) Adsorbed product molecules are desorbed from the catalyst surface; (v) Product molecules are departed from the catalyst surface by diffusion. Among those processes, (i) and (v) are physical processes, (ii) and (iv) are chemisorption phenomena, and (iii) is a chemical reaction process. That is adsorption-reaction-desorption process.

2.2. Platinum/Non-Homogeneous Catalytic Hydrogenation

Because of their carbon neutrality, substances make excellent renewable resources for the manufacture of fuels and chemicals. One of the biomass-derived substances with the highest value-added is γ-valerolactone (GVL). It shows promises as a green solvent, a chemical intermediate for the synthesis of biomass-derived chemicals, a fuel additive, and more [9].

An example is to hydrogenating levulinic acid (LA) to form GVL. The platinum-based metal Pd has a better reactivity towards esters and is therefore used in a higher proportion in practical experiments and production.

The hydrogenation reaction can take place on the catalyst surface dispersed in the liquid phase. The solubility of hydrogen in levulinic acid increases linearly with increasing pressure when the temperature is constant. Therefore, when the partial pressure of hydrogen in the reaction system increases, hydrogen concentration on the catalytic surface also rises, which in turn speeds up the reaction rate and increases the conversion rate [10]. The higher the temperature, the greater the solubility of hydrogen in levulinic acid when the hydrogen pressure is constant.

For this catalytic hydrogenation reaction, the reaction rate is independent of the LA concentration and is positively related to the concentration of hydrogen.

2.3. Activation of Esters

(i) Solvent factor: hydrogen bonding between the substrate and the solvent activates the carboxyl group and makes the hydrogenation reaction easier.

(ii) Introduction of inorganic salt ions in appropriate amounts: e.g., Co^{2+} ions, when the ester has a certain solubility in water, the metal cations in water can coordinate with the carboxyl groups of the ester dissolved in water, resulting in a decreased charge density of the electronegative oxygen atoms, thus polarising C=O bond and facilitating the reaction [11].

(iii) Steric hindrance effect: 1) The growth of the carboxylic acid carbon chain and the increase in the size of the ester group lead to a greater steric hindrance effect, which is not conductive to the adsorption of the substrate onto the catalyst, thus reducing reactivity [3].

2) When there is an electron-withdrawing group attached to the carbon chain, it can increase the positive charge density on the carboxyl carbon atom in the substrate molecule, which can also polarise the C=O bond and facilitate the attack of the activated hydrogen on the carbon atom of the C=O bond, thus enhancing the reactivity and facilitates the increase of the reaction activity[3].

Therefore, the structural conditions for a more favorable ester are a solvent that can form hydrogen bonds, a small number of inorganic salt ions, smaller space-site resistance and substitution with electron-absorbing groups.

2.4. Problems

In recent years, the rising price of precious metals has kept the price of platinum catalysts for hydrogenation high. The following problems exist in the application of precious metal hydrogenation platinum catalysts: 1) high precious metal loading; 2) high precious metal dosage; 3) poor dispersion of precious metals; 4) high cost due to excessive precious metal dosage.

3. Transition Metal-Loaded Catalysts

Loaded catalysts are catalysts in which the active components and co-catalysts are uniformly dispersed and loaded onto a specially selected carrier. In addition to platinum-based precious metal catalysts, other types of metal complexes such as silver, copper, zinc and iron will affect the catalytic activity of the metal after loading due to the influence of factors such as lattice dispersion after loading, increased contact area and the involvement of doped atoms in the reaction.

In this section, several known process routes will be used as examples to analyze the relevant factors influencing the activity of transition metal-loaded catalysts.

3.1. Activity Influencing Factor I: Temperature

Some polyfunctional organic compounds, such as methyl glycolate (MG), are commonly applied in chemistryl and pharmacy with the chemical properties of both alcohols and esters. The disadvantages of various methods for generating MG, such as harsh reaction conditions, low yields and dependence on petroleum resources, limit the development and promotion of applications. In comparison, partial catalytic hydrogenation of dimethyl oxalate (DMO) is a simple, low-cost and environmentally friendly process with high prospects for development and application [12].

In addition to increase the thermal movement rate and collision chance of the reactant molecules, the impact of increasing the temperature on the catalyst is mainly reflected in the change of the lattice structure of the central atoms, which in turn results in the coordination number change, manifested as a change in the adsorption capacity of the core atoms of the catalyst.

Take the liquid phase catalytic reduction of oxalate as an example. When the catalyst is a specific Ag/AS loaded catalyst (AS refers to mesoporous silica nanomicrospheres with functionalized surface amino modification),as the reduction temperature increases, the Ag particle size increases, the lattice arrangement becomes more neat and orderly, and the corresponding surface atom coordination number increases [13]. Spectral analysis shows that the structural change significantly reduces DMO desorption, decreases the reaction efficiency the yield.

3.2. Activity Influencing Factor II: Loading Degree

As the catalyst loading increases, most active metal atoms on the catalyst surface exist as single atoms, and the particles become smaller and the specific surface area increases, which increases the contact area between the catalyst and the reactant during hydrogenation to a certain extent, and the reaction rate increases. However, when the loading is too high, there are a large number of metal particles on the catalyst surface, which will consume some active centers due to the excessive empty loading centers, leading to a decrease in catalyst activity, a decrease in the degree of substrate binding to the catalyst, a decrease in reaction performance and a decrease in yield.

3.3. Activity Influencing Factor III: Doping Atomic Additives

Co-catalysts, as auxiliary components, have no or weak catalytic activity of their own, but when doped with the main catalyst, they can significantly improve the performance of the catalyst and are a favorable reaction modulation strategy.

As already mentioned above, GVL is a biomass derivative of great value for applications. Distinct from the known hydrogenation reduction by LA [9], Zhu et al. prepared Cu-NiδOx/SiO_2 catalyst for the conversion of ethyl levulinate (EL), which showed long-term stability at 433 K and 3 MPa H_2 with a GVL yield of 95% [14]. After studying the reaction mechanism and reaction history, it is concluded that the reaction required a bi-functional catalyst with metal and acid sites [15]. The loading effects of metal oxides (Al_2O_3, SiO_2, ZrO_2 and TiO_2) indicated that Al_2O_3-loaded Cu-Ni had the highest activity in the intramolecular esterification reactions of EL hydrogenation to ethyl 4-hydroxy valerate (EHP) and EHP to GVL.

4. Applications of Rare Earth Metals

Rare earth metals (RE) include 17 elements of scandium, yttrium and lanthanum, which have unique chemical properties. They have unique chemical properties, such as large ionic radii, high coordination numbers, easy coordination and activation of substrates, and mostly stable +3 oxidation states, which do not easily undergo redox reactions. In addition, rare-earth-carbon (hydrogen) bonds are more ionic and have higher reactivity [16].

RE catalysts refer to the catalysts using RE compounds as active components. Due to their unique electronic structure, the corresponding rare earth metal organocomplexes show special catalytic properties in some catalytic reactions. Studies have shown that the structure of the crystals of the RE compounds or the auxiliary ligands of the complexes exerts a prominent impact on the catalytic properties of the corresponding rare earth metal compounds [17].

4.1. Structure of Central Metal Compounds

The combination of ester hydrogenation reactions with the catalytic properties of RE compounds can enhance the activity of ester-catalyzed hydrogenation. Lanthanide Lewis acid and Lewis base complexes can react with hydrogen, break non-polar H-H bonds and catalyze ester hydrogenation and carbon dioxide hydrogenation reactions.

In 2017, Guan et al. discovered a new tridentate ligand and synthesized a series of RE complexes based on this ligand, in which the side-arm group was successfully used as a Lewis base with a Lewis acidic RE center to achieve 1,4-addition reactions to α,β-unsaturated ketones and esters [18].

Zheng et al. found that oxides of rare earth metals, known as "elements of the future", can be used as promoters to modify the catalytic performance of Cu/SiO_2 catalysts in the preparation of EG by DMO hydrogenation [19]. It was found that the introduction of a suitable amount of La species facilitates the formation of active copper molecular groups in the catalyst, and the introduced La species closely contacts and interacts with the Cu groups before and after the activation of the catalyst, which will improve the copper dispersion (increase the number of contact sites) and active copper surface area (increase the specific surface area) of the catalyst to a certain extent, and endow the catalyst with better thermal stability.

4.2. Ligand Variations

Altering the coordinating system enables the production of catalyst specific to a given reaction. Biodegradable polymers having numerous uses include polypropyleneglycerides. The most practical and simple way to create polypropylene glycerides is through the ring-opening hydrogenation polymerization of propylene glycerides, and rare-earth metal organocomplexes exhibit high catalytic activity for this process as well as promising prospective applications. This complex can effectively catalyze the ring-opening polymerization of L-propyl cross-ester and D, L-propyl cross-ester to obtain high relative molecular mass poly-propyl cross-ester [20].

5. Conclusion

The optimization of ester-catalyzed hydrogenation routes is a widely discussed topic as a reaction with important practical applications. Precious metal catalysts for ester hydrogenation show good performance under milder conditions, but limited applications as a result of their short lifespan, high cost, and very difficult separation of catalyst from product. A positive trend for the growth of this process in the future is the creation of novel, reasonably priced catalysts that are good performers under benign conditions.

Therefore, future research directions can be summarised as follows.

(1) Strengthen the basic theoretical research on structure and performance to meet practical production applications.

(2) Make the existing advantageous performance more obvious.

(3) Improve the product deficiencies and thus upgrade them, such as reducing the content of organic solvents and optimizing curing conditions, etc.

(4) Multi-functionalisation of products, such as increasing biodegradability, anti-bacterial properties and breathability, etc.

(5) Explore the development of new varieties actively, optimize production processes and reduce production costs.

References

[1] Xing, Q. et al. Fundamental Organic Chemistry. Beijing, Peking University Press, 2016.

[2] Li, J.J. and Rong, G. Name Reacitons--A Collection of Detailed Mechanisms and Synthetic Applications. Beijing:Science Press, 2011.

[3] X.J.Zheng,et al. Factors affecting the activation of carboxyl groups in ester hydrogenation reactions[J]. Journal of Physical Chemistry,2010,26(10):2699-2704.

[4] P.P. Upare, et al. J. Selective hydrogenation of levulinic acid to γ-valerolactone over carbon-supported noble metal catalysts[J]. Ind.Eng. Chem. 2011, 17: 287–292.

[5] W.H. Luo, U. Deka, A.M. Beale, et al., Ruthenium-catalyzed hydrogenation of levulinic acid: Influence of the support and solvent on catalyst selectivity and stability. J. Catal. 2013, 301 (2013): 175–186.

[6] W.X. Cao, et al. UiO-66 derived Ru/ZrO 2@ C as a highly stable catalyst for hydrogenation of levulinic acid to γ-valerolactone[J]. Green Chem. 2017, 19: 2201–2211.

[7] K. Yan, T. Lafleur, C. Jarvis, G. Wu, Clean and selective production of γ-valerolactone from biomass-derived levulinic acid catalyzed by recyclable Pd nanoparticle catalyst[J]. J. Clean. Prod. 2014, 72: 230–232.

[8] Y. Zhang, C, et al., Self-assembled Pd/CeO_2 catalysts by a facile redox approach for high-efficiency hydrogenation of levulinic acid into gamma-valerolactone[J]. Catalysis Communications, 2017, 93: 10-14.

[9] Li, Y. et al. Synthesis of γ-valerolactone from ethyl levulinate hydrogenation and ethyl 4-hydroxypentanoate lactonization over supported Cu-Ni bimetallic, Bifunctional Catalysts, Journal of Industrial and Engineering Chemistry, 2022, 107, pp. 215–223.

[10] ZHANG Jianwei,et al. Reaction kinetics of hydrogenation of levulinic acid to γ-valerolactone[J]. Journal of Beijing University of Chemical Technology (Natural Science Edition),2010,37(05):25-29.

[11] ZHENG Xiao-Juan,et al. Activation Factors for the Carboxyl Group in the Hydrogenation of Carboxylic Esters[J]. Acta Phys. -Chim. Sin., 2010, 26(10): 2699-2704.

[12] LI Xiangxiang, ZHU Yi 'an, ZHOU Jinghong, ZHOU Xinggui, LI Wei. Study on the Mechanism of Hydrogenation of Dimethyl oxalate to methyl glycolate Catalyzed by Silver and Copper [J]. Natural Gas Chemical Industry (C1 Chemistry and Chemical Industry),2018,43(06):17-23.

[13] DONG Guilin, LUO Zuwei, CAO Yueqiang, ZHOU Jinghong, LI Wei, ZHOU Xinggui. Effect of liquid-phase reduction temperature on performance of silver-silica catalysts for hydrogenation of dimethyl oxalate to methyl glycolate[J]. CIESC Journal, 2022, 73(1): 232-240

[14] J. Zhu, Y. Tang, K. Tang, Enhanced hydrogenation of ethyl-levulinate to γ-valerolactone over Ni δ O x stabilized Cu+ surface sites[J]. RSC advances, 2016, 6(90): 87294-87298.

[15] Z. Yu, X. Lu, H. Bai, J. Xiong, W. Feng, N. Ji. In Situ Generated Et3SiI as a Metal-Free Catalyst for the Room-Temperature Synthesis of γ-Valerolactone from Levulinic Acid[J]. Asian Journal of Organic Chemistry, 2022, 11(12): e202200650.

[16] Yiwen Guan, et al. Progress in Rare-Earth Metal-Based Lewis Pair Chemistry[J]. Chinese Journal of Organic Chemistry, 2022, 42(5): 1326-1335.

[17] QIAN C T, WANG C H, CHEN Y F. Sixty years of the chemistry of rare-earth organometallic complexes[J]. Acta Chim Sin,2014, 72(8): 883-905.

[18] Xu P,et al. Frustrated Lewis Pair-Like Reactivity of Rare-Earth Metal Complexes: 1, 4-Addition Reactions and Polymerizations of Conjugated Polar Alkenes[J]. Chemistry-A European Journal, 2017, 23(6): 1263-1267.

[19] Zheng, Xinlei.. Rare earth oxide modified and bimetallic copper-based catalysts in the reaction of dimethyl oxalate selective hydrogenation to ethylene glycol. (Doctoral dissertation, Xiamen University). 2014.

[20] Hong-Xia CHEN,et al. Synthesis,Characterization and Catalytic Activity of Benzylamine-bridged Bis(phenolato)lanthanide Complexes[J]. Chinese Journal of Applied Chemistry, 2022, 39(5): 843-851.