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Analysis on the catalytic performance of catalysts and cost-effectiveness and selectivity of methanol carbonylation

Hongxiang Ren

Insight Academy of Canada, 1039McNicoll Ave Unit 200, Toronto, ON, Canada

Rhxrhx66@163.com

Abstract. Methanol is an essential raw chemical that is also a source of environmentally friendly energy for use in automobiles and other uses. It is one of the most important organic raw materials that is used in the manufacturing of a wide variety of organic compounds, such as chloromethane, methylamine, and dimethyl sulfate, among many others. It is one of the raw materials used in the production of dimethyl terephthalate, methyl methacrylate, and methyl acrylate, in addition to being a raw material for pesticides (insecticides, acaricides), pharmaceuticals (sulphonamides, co-trimoxazole, etc.), and other chemicals (such as sulfonamides and co-trimoxazole, for example). This paper investigates the catalytic performance of various catalysts for methanol carbonylation through a method of literature review. The purpose of the study is to determine which catalyst offers the most value for the price. In addition to that, the research investigates the efficiency in terms of cost and the selectivity of the methanol carbonylation process.

Keywords: methanol, carbonylation, catalyst, methyl methacrylate.

1. Introduction

Methanol is both a clean source of energy for automobiles and a vital raw ingredient. In actuality, acetic acid is a very important chemical raw material utilized in the creation of numerous key chemical products, such as fibre acetate and vinyl acetate for use in the textiles, copolymer resins, pharmaceutical, and food industries [1]. The fibre, copolymer resin, medicinal, and food sectors utilize it. It is intimately connected to people's lives. The fermentation of grains, the oxidation of acetaldehyde, the liquid phase oxidation of low carbon burning hydrocarbons, and the carbonylation of methanol are the primary sources of acetic acid [2]. At atmospheric pressure and 60°C, 95% of acetaldehyde is converted by oxidation of acetaldehyde [3]. In this process, however, organic mercury catalysts have been phased out because to their severe environmental impact. The direct oxidation of olefins is constrained by the low feedstock conversion (butane, petroleum, etc.), the complexity of the product separation process, and the high cost. Since its development and implementation in the late 1960s, the low-pressure carbonyl synthesis of acetic acid from methanol, which was invented by Monsanto in the United States, has become the predominant technique of acetic acid production worldwide. $CH_3OH + CO == CH_3COOH$ The advantages of the methanol process include a choice of raw material pathways, with coal coke, natural gas, and heavy oil as the primary raw materials, notably for coal chemistry, as well as few by-products, reduced triple waste, and straightforward production. The catalyst is extremely active, has a lengthy lifespan, and is employed rarely. Rhodium catalysts are extremely expensive, and many uncertainties remain regarding the economics of this approach and the catalysts' catalytic efficacy. In numerous investigations. Frequently, the economics of a catalyst are inversely proportional to its catalytic efficiency. Through a literature study, this paper examines the catalytic performance of catalysts for methanol carbonylation in an effort to identify the most cost-effective catalyst. In addition, the research examines the cost-effectiveness and selectivity of methanol carbonylation.

2. Mainstream methods of methanol carbonylation

BP Chemicals acquired the catalyst technology for the rhodium-based carbonylation of methanol to acetic acid from Monsanto in 1986 and has worked to enhance it over the years. In 1996, it was announced that a novel CATIVA acetic acid method based on methanol carbonylation had been invented, employing iridium metal as the primary catalyst, with the option of adding rhenium, ruthenium, and osmium as auxiliary catalysts. At 120°C, an aqueous solution of carbonylated iridium $[Ir(CO)_{12}]$, hydriodic acid, and acetic acid was refluxed to produce the novel catalyst. The Cativa process for carbonylation of methanol to acetic acid has the following benefits over the typical Monsanto rhodium-based catalyst technology: Iridium is much less expensive than rhodium; iridium-catalyzed systems are more active than rhodium-catalyzed systems; have fewer reaction by-products; and can function at lower water contents (below 8% for the Cativa process against 14-15% for the Monsanto process) [4].

Using the Monsanto methanol carbonylation to acetic acid method, Celanese Chemical constructed a major acetic acid production facility in 1978. Based on this, the company successfully developed a new method to create Celanese low water content acetic acid in the early 1980s. Core to the low water content acetic acid technique is the addition of high concentrations of inorganic iodides, primarily lithium iodide, to a rhodium-based catalyst in order to improve the catalytic system's stability. The inclusion of lithium iodide and iodomethane reduces the water content of the reactor significantly while retaining a high reaction rate, resulting in a considerable reduction in separation costs for the new method [5]. Celanese's low water acetic acid technique is identical to the old Monsanto methanol carbonylation process, although this technology has advantages and downsides. The principal technical advantages are improved capacity and lower engineering and investment costs; the downsides are that the use of high concentrations of iodide salt might result in increased corrosion and increased iodide salt residues in the product. High concentrations of iodide salt may be detected in the final acetic acid product.

3. Selectivity of methanol carbonylation

In the presence of a drilled (or germanium) diallyl complex catalyst, the methanol carbonylation process yields acetic acid from the reaction of CO and methanol. The carbonylation of methanol to acetic acid is an industrially significant process. Its precursor consists of two components: a soluble rhodium complex and an iodide. The discovered germanium catalyst offers high conversion and selectivity for methanol. An aqueous solution of $RhCl_3$ - 3H2O and HI is dissolved in an aqueous solution of acetic acid to generate it. Carbonylation of methanol can be used to make a variety of compounds. There are also numerous methods for producing methanol carbonylation. For instance, BASF developed the first cobalt-based catalyst in 1960 (based on the work of Reppre et al.) utilizing cobalt carbonyl as the catalyst and iodomethane as the co-catalyst, which had the disadvantages of harsh reaction conditions (65 MPa, 250°), low selectivity of acetic acid (87% in methanol), and numerous by-products, and thus was not industrialized. Today, low molecular rhodium complexes are utilized as catalysts for the carbonylation of acetic acid, and rhodium-based catalysts manufactured by Monsanto in the United States have been effectively implemented in industrial production. Due to the high cost of rhodium, however, there has been great interest in researching non-rhodium-based catalysts for the carbonylation of methanol [5].

4. Multi-phase catalysis for the carbonylation of methanol

Many more catalysts exist. Multiphase system catalysts, which are separated into two types of catalysts, are one example. Iodide-promoted liquid-solid and gas-solid reaction system catalysts.

In 1998, Chiyoda and UOP developed the Acetica TM Rh-loaded catalyst for liquid-solid catalysis. At 160-180 °C and 3-6 MPa, the catalyst system produced by immobilizing Rh(I) with poly(vinyl pyridine) resin exhibited selectivity and yield of acetic acid comparable to the Monsanto process. In addition, an alkali metal iodide promoter is not required to stabilize the primary catalyst Rh(I); lower water content in the reaction system leads in less by-product generation; low water content decreases the quantity of HI produced and reduces equipment corrosion. The reaction conditions and stability of solid carbonylation catalysts put on oxides are significantly harsher and less stable than those loaded on polymers. Blasio et al. examined the multiphase methanol carbonylation reaction in solution using Rh catalysts solidly loaded on ZrO_2 or activated carbon (AC) or crosslinked with side-group PPh2 groups (SDT) on polystyrene; nevertheless, the loss of the solidified catalysts was more severe. Ru, Co, Fe, and Ni loaded on AC have also been studied, and their activity in methanol carbonylation processes has been demonstrated. However, the reaction conditions are significantly more stringent than for liquid phase Rh or Ir catalysts. The primary drawbacks of catalyst systems loaded with oxides are catalyst loss, limited reactivity, and severe reaction conditions [6].

Iodide promoted catalysts for gas-solid reaction systems: S.J. Uhm et al. examined activated carbon, clay, alumina, silica, phosphate and other carriers and experimentally proved that activated carbon was the best carrier. Metal catalysts with activated carbon as a carrier have the advantage that the reaction can catalyze the carbonylation of methanol at atmospheric pressure, but the activity is low. The order of activity of group VIII metal elements loaded on activated carbon for methanol carbonylation is Rh > Ir > Ni > Pd > Co > Ru > Re [7]. In addition, the metal Pd can increase the lifetime of the methanol carbonylation catalyst Ni/AC. Although the gas-solid carbonylation catalysts with activated carbon as the carrier have certain activity, activated carbon has weaknesses such as low mechanical strength and poor thermal stability.

5. The improvement and development of methanol carbonylation technology

The first is a double reactor tandem process, the second reactor in series can make the first reactor is not fully reacted raw materials fully reacted to improve the reaction efficiency, and reduce the load of the separation and refining and tail gas recovery system. This technology has advanced domestically and internationally, but its characteristics vary. In order to solve the problem of catalyst precipitation, the domestic Southwest Chemical Research and Design Institute adds a converter and reduces the water content in the reaction solution to improve the reaction conversion rate, so that the rhodium catalyst, which is easy to decompose and precipitate, can withstand heating; the evaporation process is used when removing the crude acetic acid, which differs from the conventional BP procedure. The absorbent for tail gas absorption is methanol, which has a stronger absorption effect than acetic acid, is less absorbent, and is less corrosive to equipment. The gas-phase methanol carbonylation process attempts to eliminate the shortcomings of the liquid-phase approach, such as catalyst loss, equipment corrosion, and the difficulty of product separation and refining. The low-pressure methanol carbonylation method has been continually refined and enhanced in terms of catalyst, process, and equipment, which has contributed favorably to the large-scale production plant, energy consumption reduction, cost reduction, and competitiveness enhancement [3].

The carbonylation of methanol to acetic acid is the current favored technique for large-scale acetic acid production, accounting for over 60% of worldwide acetic acid production capacity, and will continue to increase its share as the chosen technology for new large-scale facilities. Both the Celanese low water content process created by Celanese and the CATIVA process developed by BP Chemicals have enhanced catalyst performance and decreased water content in the reactor, resulting in substantial outcomes. They are now advanced and mature acetic acid production methods that have been extensively implemented in the technical transformation of existing acetic acid plants, resulting in a significant increase in plant capacity. China has abundant natural gas and coal resources, which serve as the foundation for the country's growth of natural gas, coal-bed methane, and coal-to-methanol technologies. The methanol carbonylation process accounts for less than thirty percent of production and requires immediate transformation.

Low-pressure carbonylation of methanol offers numerous benefits and dominates the synthesis of acetic acid, but the Monsanto technique has two significant technical challenges: germanium catalysts, concealed features, and corrosive equipment. Listed below are several enhancements to the Monsanto catalyst process. The addition of other components to the rhodium catalyst to increase the stability and activity of the catalyst, the use of solid catalysts to facilitate the separation of product and catalyst, and the reduction of catalyst loss are the primary areas of improvement. Union Carbide, for instance, utilized $[Rh(CO)_2CL]$. -Ph2P(CH2)2-LiI-MeL complexes for the low-pressure carbonylation of methanol at 115°C and 7.0 MPa were nearly 100 percent selective for acetic acid [8].

6. Other metal homogeneous catalyst systems

Although rhodium and iridium catalysts have demonstrated good catalytic effects in the homogeneous carbonylation of methanol for the synthesis of acetic acid, the catalyst stability is poor and the cost is high; consequently, a significant amount of research has been conducted on other metal catalyst systems. Tonde et al. evaluated the $Pd(OAc)_2$ - HI - PPh_3 catalyst system [9], which demonstrated a strong catalytic effect for carbonylation at 175 °C, where PPh3 increased the high temperature stability of the catalyst; however, the catalytic impact was somewhat distinct from that of the Rh catalyst system. In the carbonylation of acetic acid from methanol, cobalt and nickel catalytic systems have been studied continuously. The Co catalytic system, which was originally marketed by BASF in the 1960s, was the first catalytic system for the carbonylation of acetic acid from methanol, although it needed the maintenance of a high pressure. When Ni salts are combined with metal iodides such as alkali metals, tin, molybdenum, and organophosphates, the catalytic effect significantly increases at lower auxiliary concentrations and is partially suppressed at higher auxiliary concentrations, with phosphine being the most effective catalyst for Ni catalysts [10-11]. However, the issue of $Ni(CO)_4$'s toxicity has not been satisfactorily resolved, restricting its industrialisation. Guzman-Jimenez et al. studied the homogeneous catalytic carbonylation of methanol with $[Et_4N]^2[Fe^-_3 (CO)_9E]$ (E = S, Se, Te) for the synthesis of acetic acid [12], and showed that the effect of Fe-Te > Fe-S > Fe-Se in the carbonylation of methanol at a CO pressure of 1200 psi (ca. 8. 175 MPa) and 90 °C. Non-Rh and non-I catalysts were more effective in the carbonylation of methanol at low levels of CO. However, the low methanol conversion and acetic acid selectivity, the high by-products, and the harsh temperature and pressure conditions are not of high value for industrial application at present, and additives and new ligands are needed to improve the catalytic performance. In summary, the shortcomings of homogeneous catalysts have been addressed by the addition of co-catalysts and ligands and the synthesis of new coordination metal compounds. In recent years, ionic liquids have attracted attention for their low boiling point, low vapor pressure, chemical inertness and efficient heat transfer properties, and have been investigated in various ways as green solvents and catalysts. For example, Eastman reported on the effect of ionic liquids on carbonylation catalyst systems [13], and investigated the effect of different structures of ionic liquids on the carbonylation reaction rate, which for iridium-based catalyst systems is mainly due to the ionic liquid binding the iodide ions in the system, thereby increasing the carbonylation reaction rate. At the same time, when ionic liquids are used to facilitate the catalytic reaction, a special degassing device (Vapor take-off) can be designed to combine the reaction and product separation steps in the same unit operation, avoiding the need to transfer the catalyst and product together.

7. Conclusion

The process of carbonylating methanol is the subject of this study. This approach is not particularly popular in everyday life, but it is quite widespread in the business world. It is not possible to test more substances for catalytic capabilities due to the high cost of catalysts and the impossibility of doing individual tests on them. In order to replace the use of rhodium catalysts, a more appropriate catalyst must already exist. Because of this, the report does not provide an exhaustive analysis. In the not too distant future, additional study will be conducted in this area.

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