



Research article

Reductive carbonylation of methanol for ethanol production in Rh-Ru-dppp-methyl iodide catalytic system under mild conditions – The effect of lithium salts and catalyst composition

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ARTICLE INFO

Keywords:

Methanol
Reductive carbonylation
Homogeneous
Rhodium
Ethanol

ABSTRACT

Reductive carbonylation of methanol is a potential process for ethanol production, but the reaction temperature is always higher than 190 °C and reaction pressure higher than 19 MPa. Due to the corrosions of the catalytic system, the reaction conditions, especially the pressure limited commercial applications of this process. The catalytic system consists of rhodium, ruthenium, dppp and methyl iodide, and was investigated for reductive carbonylation of methanol to ethanol under 6.0 MPa at 120 °C, and it exhibited an attractive catalytic activity. By comparing the products selectivity and the turnover frequency (TOF) of the catalytic systems, the role of each component in the catalytic system has been investigated. Rhodium catalyst was found to catalyze methanol reductive carbonylation for acetaldehyde formation, and ruthenium catalyst was responsible to catalyze hydrogenation of acetaldehyde to ethanol. The dppp can coordinate to rhodium and form a molecule rhodium active species, which enhanced the stability and solubility of the rhodium catalyst under the relatively low reaction pressure. The methyl iodide can promote the split of a carbon-oxygen bond of methanol, thus accelerate the reaction process even at 120 °C. The synergy effects of these catalyst compositions give rise to the ethanol formation under the relatively mild condition. Additionally, reaction conditions, catalytic system proportional and presence of lithium salts were combined to tune the TOF and ethanol production. Properly increasing initial methyl iodide addition, dppp/Rh mole ratio, H₂/CO mole ratio, reaction temperature and pressure can accelerate the TOF. Raising Ru/Rh ratio and reaction temperature were in favor of acetaldehyde hydrogenation to ethanol. High H₂/CO and dppp/Rh ratio can suppress the acetic acid formation. This work could provide a deeper understanding for further optimization to enhanced ethanol production.

1. Introduction

As public concern about environmental pollution increases, ethanol-fuel blends have recently attracted interests from academia and industry because of the potential to promote fuel combustion [1–3] and thus reduce particulate and CO emissions [4–7]. Traditionally, ethanol has been mainly produced from ethylene hydration and biomass (mainly sugar cane and maize) fermentation [8], but low energy efficiency, political uncertainty and societal issues have guided the research efforts into development of alternative feed stocks/routes for its production.

Converting synthesis gas (syngas) to ethanol has been considered as a possible route owing to the convenient sources of syngas. Particularly, syngas from cellulosic biomass gasification is environmentally cleanly and sustainable [9]. Four R&D processes involving direct and indirect routes for producing ethanol from syngas are shown in Fig. 1. Due to

the kinetics reasons, the direct synthesis of ethanol from syngas (route 1) suffers from low yield or poor selectivity [10–12]. Al-Megren et al. [13] prepared a molybdenum based catalyst for synthesizing high alcohols from syngas. The selectivity to alcohol was 72.5% with a conversion of 14.1%, and the best catalyst achieved 32.3 wt% selectivity to ethanol in the alcohol. Although higher conversion in each step could be obtained with indirect routes (route 2 [14–16] and 4 [17,18]), too many intermediate steps make the cost increase and the commercial application limited. Alternatively, reductive carbonylation of methanol (route 3) [19–21] seems more attractive for its higher ethanol yield than direct process and the least intermediate steps among the indirect processes.

Gerald S. Koerner reported that [22] Co₂(CO)₈ could catalyze reductive carbonylation of methanol under 26.9–31.7 MPa, 190 °C with a turnover frequency (TOF) of ca. 25 mol/(mol Co)·h⁻¹. The highest selectivity of ethanol was 26.4%. Subsequently, M. Röper [23] prepared

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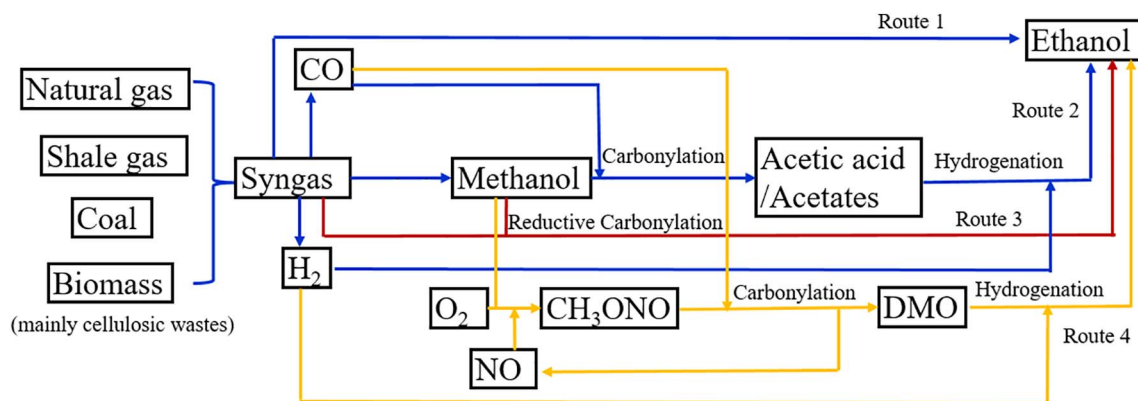


Fig. 1. Routes of ethanol synthesis from syngas.

a Co-P-I catalyst system, which was used in the reaction under 100 MPa, 190 °C. The highest selectivity of ethanol reached 9.7%. After that, G. Doyle [24] developed a Co-Ru-P-I catalyst system, the TOF reached 425 mol/(mol Co)·h⁻¹ under 27 MPa, 220 °C. The highest selectivity to ethanol was 86%.

As described above, the reaction temperatures were always higher than 190 °C to obtain an acceptable reaction rate. Meanwhile, the reaction pressures were usually higher than 19 MPa to enhance the stability of active species (i.e. metal carbonyl complexes) under the high reaction temperature. However, the high pressure led to much cost in both equipment investment and operation due to the corrosion of the catalytic and products system (e.g. halogen and acetic acid), and thus limited the industrial application of this process.

Fortunately, Moloy et al. found that Rh-Ru-diphosphine-methyl iodide catalytic system showed high selectivity to ethanol/acetaldehyde under relatively low pressure (6.89 MPa) [20,25,26], which opened a new avenue for this process under mild condition. However, the effect of reaction condition and catalyst composition has not been systematically studied, and the role of each catalyst composition is still not fully understood. Moreover, in the rhodium-catalyzed carbonylation of methanol/methyl acetate process, lithium salts were always used to stabilize the catalytic system and improve the TOF [27–29]. Up to now, the effect of lithium salts has been not studied in the rhodium-catalyzed reductive carbonylation of methanol, and even little work has been carried out so far to develop this catalytic system further, especially under the mild condition.

In this work, the roles of catalyst compositions and operating parameters on TOF and products selectivity were systematically investigated. The effects of lithium salts were also studied. These findings of this study are helpful and meaningful for further improving the catalytic performance of the Rh-Ru-dppp-methyl iodide catalytic system.

2. Experimental

2.1. Reagents

Dicarbonyl (2,4-pentanedionato) rhodium(I) (Rh(CO)₂(acac) 99%) and ruthenium (III) chloride hydrate (RuCl₃·xH₂O Ru > 37%) were purchased from Sino-platinum Metals Co CHN. 1,3-bis (diphenylphosphino) propane (dppp 99%) was purchased from Puyang Huicheng Electronic Material Co CHN. Methanol (MeOH 99.5%), lithium carbonate (Li₂CO₃ 99%), lithium iodide (LiI 99%), lithium acetate (CH₃COOLi 98%) and methyl iodide (CH₃I 98%) were purchased from Sinopharm Chemical Reagent Co CHN. Carbon monoxide (CO 99.99%) was purchased from Foshan Huate Gas Co CHN and hydrogen (H₂ 99.99%) was purchased from Baosteel Gases Co CHN.

All of reagents were used without purification.

2.2. Experimental procedure

In a typical experiment, known quantities of catalyst precursors, ligand, methyl iodide and methanol were charged into a 500 mL titanium alloy magnetically stirred autoclave. Each reactant was weighed on a BH-300 electronic balance (with ± 0.005 g uncertainty) manufactured by Excell Precision Co. LTD. Then the reactor was flushed with CO (to remove air) and pressurized to 3.0 MPa with the desired H₂/CO ratio. A precision pressure meter with ± 0.1 MPa accuracy was employed to record any changes in pressure. The contents were heated to the required temperature in 30–50 min with the agitation speed of 350 ± 10 rpm.

The temperature of the reaction solvent system was measured with a K-type thermocouple (with ± 2.2 °C uncertainty) placed at the center of the autoclave. Keep the reaction pressure fixed by pressurizing with the desired H₂/CO ratio syngas.

At the end of the reaction, the reactor was cooled to room temperature, the pressure was vented and the liquid products were collected.

2.3. Analytical methods

The liquid phases were analyzed using a gas chromatograph (Agilent 7890A) equipped with an HP-5 column (30 m × 0.32 mm × 0.25 μm). A flame ionization detector (FID) operation at 150 °C was utilized with nitrogen as carrier gas. The column oven temperature was maintained at 40 °C for 3 min, then increased to 90 °C at a rate of 5 °C min⁻¹, and held there for 3 min. The products were qualitatively analyzed by GC/MS using the above analytical methods and quantified using acetonitrile as the internal standard. The products compose of ethyl methyl ether (MeOEt), diethyl ether (Et₂O), ethanol (EtOH), ethyl acetate (EtOAc), methyl acetate (MeOAc), acetic acid (AcOH), 1,1-dimethoxyethane (MeC(MeO)₂H) and 1-ethoxy-1-methoxyethane (MeC(MeO)(EtO)H). Each correlation coefficient of the products was over 0.999 for standard curves. Additionally, the product analysis was done by the Agilent ChemStation software installed on the computer.

The TOF is defined as a number of moles of consumed methanol per mol of introduced rhodium per hour:

$$\text{TOF (mol/(mol Rh)·h}^{-1}) = \frac{\sum \text{moles (products } x) \times (n)}{(\text{moles of rhodium}) \times (\text{reaction time, } h)} \times 100\% \quad (1)$$

where n is the number of methyl groups originating from methanol and incorporated in product x.

The selectivity is calculated in the usual way [20,25], as seen in Eqs. (2)–(5).

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