Catalysis Communications 68 (2015) 46–48

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Ruthenium trichloride as a new catalyst for selective production of dimethoxymethane from liquid methanol with molecular oxygen as sole oxidant

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ARTICLE INFO

Article history:
Received 7 March 2015
Received in revised form 23 April 2015
Accepted 26 April 2015
Available online 28 April 2015

Keywords:
Dimethoxymethane
Methanol
Liquid phase oxidation
$RuCl_3$

ABSTRACT

Dimethoxymethane was first synthesized from methanol with a liquid phase intermittent process which only used molecular oxygen as the sole oxidant. $RuCl_3$ was proved to be an efficient catalyst as it posses the ability of oxidizing methanol and Lewis acidic which promotes the oxidation of methanol to formaldehyde and then methanol condensed with formaldehyde to form dimethoxymethane at Lewis acid site.

1. Introduction

Dimethoxymethane (DMM), or methylal, is an excellent green solvent and chemical intermediate because of its extremely low toxicity, low boiling point, and good solubility and intersolubility with water. It has been widely used in pharmaceutical and perfume industries and organic synthesis, and it is also a potential diesel additive which can decrease the soot emission [1].

DMM is usually produced by a two-step process in the industry: the first step is the oxidation of methanol to formaldehyde over Fe–Mo or Ag catalyst, and the second step is the condensation of formaldehyde obtained from the first step with methanol in the presence of acids [2,3]. In consideration of the long technological processes which caused the inevitably high cost, a lot of effort have been made and most focused on one-step selective oxidation of gaseous methanol to DMM. And lots of selective oxidation catalysts have been reported such as crystalline $SbRe_2O_6$ [4–6], Re/γ–Fe_2O_3 [7], ReO_x/TiO_2 [8], RuO_x/SiO_2 [9], heteropolyacid [10,11], Cu–ZSM-5, Fe–Mo–O [12], V_2O_5/TiO_2 [13–18] and so on. Among these catalysts mentioned above, ReO_x/TiO_2 [8], Fe–Mo–O [12] and V_2O_5/TiO_2 [13–18] show better catalytic performance for the selective oxidation of methanol to DMM. However, the activity of those catalysts were evaluated in a continuous flow fixed bed reactor, except the Nb_2O_5 catalyst reported by N. T. Prado [19] can make the reaction carried out in a sealed glass reactor using H_2O_2 as oxidant.

Comparing with the gas phase continuous process, the liquid phase intermittent process spares the gasification of raw materials and condensation of products, so the liquid phase intermittent process is energy saving. In this work, we successfully implemented the selective oxidation of methanol to DMM in the liquid phase intermittent process, and only use molecular oxygen as the sole oxidant. we also found that $RuCl_3$ is an effective and potential catalyst because of its special chemical properties that it can effortlessly adopt various formal oxidation states from -2 to $+8$ in chemical bonds, therefore giving rise to many compounds with interesting and often unique properties [20].

According to the reaction mechanism reported by other researchers [8], the oxidability and acidity are the essential properties of the catalyst for the selective oxidation of methanol to DMM. Because of the oxidability of catalyst, firstly methanol will be oxidized to formaldehyde and then formaldehyde will be oxidized to formic acid, during this process methanol and formaldehyde can condensate to DMM on the acid sites of catalyst and formic acid and methanol can esterify to methyl formate. Thus, the possible by-productions of direct selective oxidation of methanol to DMM are formaldehyde, formic acid and methyl formate, so in order to decrease the formation of those by-productions, appropriate proportions of oxidability and acidity of catalysts are needed. Ruthenium chloride is a mild Lewis acid which can promote the condensation of formaldehyde with methanol to DMM, and the Ru^{3+} that existed in methanol can oxidize methanol to formaldehyde [21,22].

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http://dx.doi.org/10.1016/j.catcom.2015.04.031
1566-7367/

Thus Ruthenium chloride is a potential catalyst for selective oxidation of methanol to DMM.

2. Experimental

The catalytic reaction for the selective oxidation of methanol was carried out in a 100 ml high pressure autoclave made of stainless steel-316 L having facilities for gas inlet, outlet, temperature controlled heating and variable agitation speed. The materials used in this reaction included $RuCl_3 \cdot nH_2O$, $FeCl_3 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $ZrCl_4$, $ZnCl_2$, methanol (all from Sinopharm Chemical Reagent Co., Ltd, China) and O_2 were purchased from commercial source. In a typical reaction, 20 ml methanol (MeOH) and quantitative metal chloride were added in the autoclave. After replacing the air in the autoclave by O_2, certain initial pressure of O_2 was filled into the reactor, and then the reaction was proceeded at certain temperature for 2.5 h. After the reaction, the liquid samples were immediately analyzed by GC (GC-14B, Shimadzu, Japan) with FFAP column and FID detector.

3. Results

Table 1 shows the results of catalytic performance of different metallic chlorides for the selective oxidation of methanol to DMM. As shown in Table 1, when 1 g of common metallic chlorides like $FeCl_3$, $NiCl_2$, $ZrCl_4$, $ZnCl_2$ was used as catalyst respectively, the conversion of methanol (<4%) was very low. But when 0.001 g $RuCl_3$ was used as catalyst, the conversion of methanol increased to 13.8%. With the increase of the amount of $RuCl_3$, the conversion of methanol and the selectivity of DMM increased rapidly. When the amount of $RuCl_3$ increased to 0.1 g, which was less one-tenth of the amount of other metallic chlorides, the conversion of methanol was rapidly increased to 37.8% and the selectivity of DMM was increased to 84.3%. These results indicated that $RuCl_3$ was a new high-efficiency catalyst for selective oxidation of methanol to DMM in the liquid phase intermittent process and only use molecular oxygen as the sole oxidant, due to the ability of oxidizing methanol of Ru^{3+} reported by Bilgrien C that Ru^{3+} can oxidize the alcohols to aldehydes and ketones and translate to Ru^{2+} and then Ru^{2+} would be oxidized to Ru^{3+} by O_2 [22], and the Lewis acidic of $RuCl_3$ which is beneficial for the oxidation of methanol to formaldehyde and the condensation of methanol with formaldehyde. Other common metallic chlorides also were Lewis acid which can promote the condensation of methanol with formaldehyde, but these metallic chlorides can't oxidize methanol as much as $RuCl_3$, so the conversion of methanol was low when common metallic chlorides were used as catalysts.

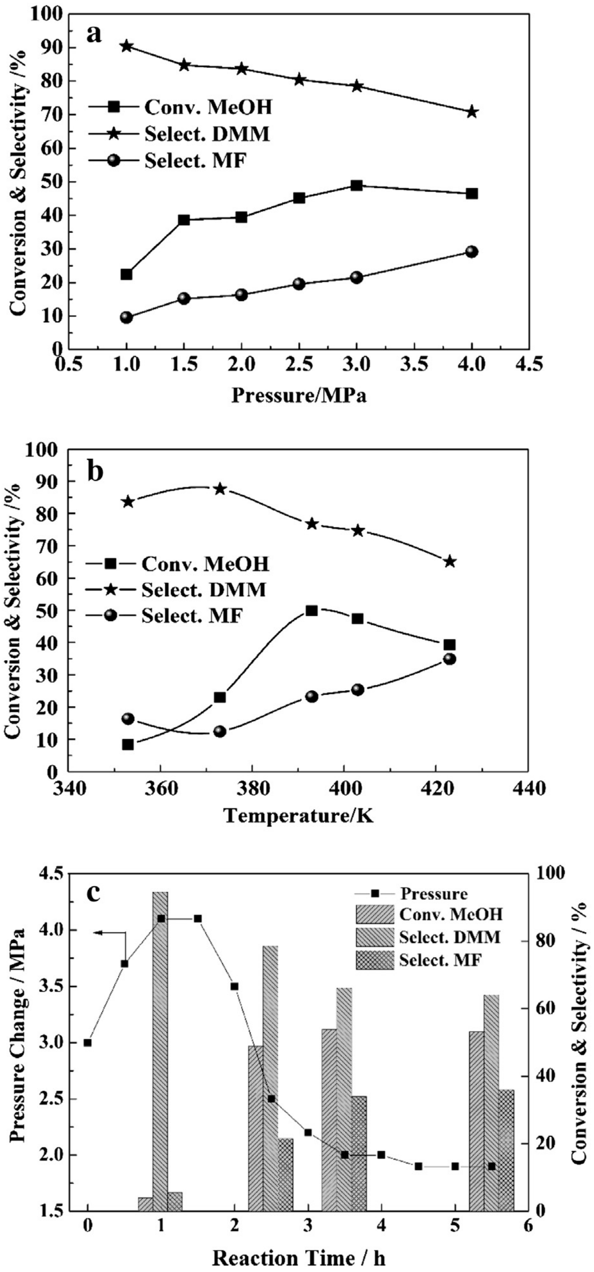

Fig. 1. Selective oxidation of methanol to DMM on $RuCl_3$ catalyst: (a) initial pressure dependence, (b) temperature dependence, and (c) reaction time dependence. Reaction conditions: 0.1 g catalyst, 20 ml methanol.

Fig. 1 shows the results of the selective oxidation of methanol to DMM over $RuCl_3$ catalyst. As shown in Fig. 1(a), the conversion of methanol increased from 22.5% to 48.9% with the increase of initial pressure from 1.0 MPa to 3.0 MPa. And then continuing to increase the initial pressure to 4.0 MPa, there was no big change on the conversion of methanol. And it still can see that the selectivity of DMM decreased and the selectivity of MF increased slowly with the increase of initial pressure. This information can be interpreted by that the high initial pressure of O_2 added in the autoclave before reaction made more O_2 dissolve into methanol and then O_2 oxidized more Ru^{2+} to Ru^{3+} which promoted the oxidation of methanol to formaldehyde [22], at the same time, more formaldehyde would be oxidized to formic acid and finally it will promote the formation of MF because of the esterification between methanol and formic acid. Fig. 1(b) shows that the conversion of methanol was first increased from 8.4% to 49.8% with the increasing of temperature from 353 K to 393 K, and then decreased to 39.3% with further increasing of temperature to 423 K. This phenomenon was caused by that both the oxidation and condensation reactions are exothermic reactions that can be favored by raising temperature in specific

Table 1
Selective oxidation of methanol to DMM over different metallic chlorides catalysts.

Catalysts active metal	Mass of catalyst (g)	Conv. (%) MeOH	Select. (%)	
			DMM	MF
$FeCl_3$	1	3.2	33.6	66.4
$NiCl_2$	1	1.5	29.7	70.3
$ZrCl_4$	1	2.7	31.3	68.7
$ZnCl_2$	1	2.0	62.8	37.2
$RuCl_3$	0.15	43.0	78.2	21.8
	0.1	37.8	84.3	15.7
	0.05	23.0	86.5	13.5
	0.01	15.1	74.8	25.2
	0.001	13.8	69.3	30.7

Reaction condition: T = 120 °C, $P(O_2) = 2.0$ MPa, Time = 2.5 h.
MeOH: methanol DMM: Dimethoxymethane MF: methyl formate.

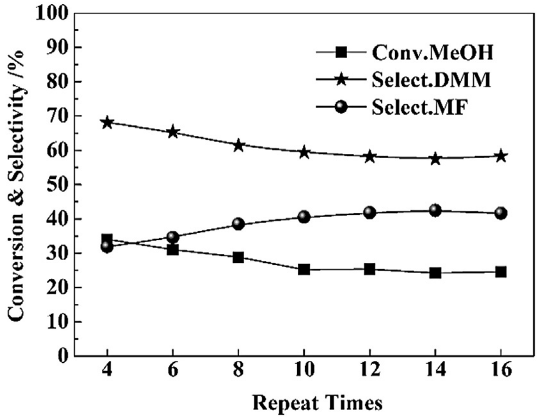

Fig. 2. Stability tests of $RuCl_3$ catalyst for selective oxidation of methanol to DMM. Reaction conditions: 0.1 g catalyst, 20 ml methanol, 2.5 h, 393K and 2.0 MPa.

range, and continuing to increase the reaction temperature, the reactions were inhibited to a limited extent.

In order to investigate the pressure changing during the reaction time, the pressure change during a 5.5 h reaction after filling 3.0 MPa O_2 into the autoclave was recorded. These results are shown in Fig. 1(c). The reaction temperature was arrived at 120 °C in 1 h, and after then it maintained at 120 °C. As shown in Fig. 1(c), the pressure in autoclave increased to 4.1 MPa from 3 MPa in 1 h when the reaction temperature was arrived at 120 °C, and then decreased rapidly to 2.0 MPa from 1 h to 3.5 h and maintained at 2.0 MPa from 3.5 h to 5.5 h. This data demonstrate that oxygen would be consumed during the reactions, and the consuming of oxygen would be stopped when the reaction proceeded in a certain degree, but the oxygen would not be depleted after reaction. With the purpose of investigating how the pressure change in the reactor and reaction time influence the reaction, we did four times reactions with the same initial pressure (3.0 MPa) and various reaction time like 1 h, 2.5 h, 3.5 h and 5.5 h which the final pressures in the autoclave at reaction temperature were 4.1 MPa, 2.4 MPa, 2.0 MPa and 2.0 MPa. As it was shown in Fig. 1(c), the conversion of methanol was less than 5% when the reaction time was 1 h. Combining with the pressure change shown in Fig. 1(c), this result indicates that the oxygen was not or less was consumed for the oxidation of methanol so that the conversion of methanol was low. Thus, the high conversion of methanol (48%) when reaction time is 2.5 h would be got due to the more oxygen had been consumed which can be seen from the rapidly decrease of the pressure in autoclave shown in Fig. 1(c). And so, further increasing the reaction time to 3.5 h and 5.5 h, the conversion of methanol (53%) was no big change because the pressure (2.0 MPa) in autoclave was no big change which indicates that no more oxygen had been consumed for the oxidation of methanol, but the selectivity of DMM was decreased and more MF formed that is perhaps caused by the long reaction time. Those experiments imply that when reaction time is 2.5 h, maximum oxygen could be consumed for the oxidation of methanol and get the highly selectivity of DMM.

Fig. 2 shows the result of the stability tests of 0.1 g $RuCl_3$ catalyst for selective oxidation of methanol to DMM. After each test, the autoclave would be opened and placed into a vacuum oven for over 12 h at 353 K to evaporate the liquid of the reaction, such as methanol, DMM, MF and water. And next test was proceeded as mentioned above without adding new $RuCl_3$ into autoclave. As shown in Fig. 2, the conversion of methanol and the selectivity of DMM declined with the increasing reused times, but after reused 10 times the catalytic performance was almost stable. It indicated that $RuCl_3$ was a potential catalyst for selective oxidation of methanol to DMM in the liquid phase intermittent process which only uses molecular oxygen as the sole oxidant. After testing for several times, $RuCl_3$ which can dissolve in methanol easily changed into a lot of black fine particles dispersing in methanol. The $RuCl_3$ may be changed into RuO_x during the reaction which causes the decreasing of methanol conversion at the beginning.

4. Conclusions

In conclusion, $RuCl_3$ is an effective and potential catalyst for selective oxidation of liquid methanol to DMM, which is first used in the liquid phase intermittent process and only use molecular oxygen as the sole oxidant. $RuCl_3$ can oxidize methanol to formaldehyde which is then condensed with methanol to produce DMM because of the mild Lewis acidic supplied by $RuCl_3$. The selectivity of DMM reached 76.8% with 49.8% conversions of methanol at 393 K and 3.0 MPa O_2 over 0.1 g $RuCl_3$.

Acknowledgments

This work was financial supported by the Special Project for the Outstanding Youth Innovation Team of Sichuan Province (2013TD0010), 1000 Talents Program of Sichuan Province and Talents program of Chengdu.

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