Catalytic reduction of N_2O with CH_4 over various Cu-SBA-15 catalysts

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ABSTRACT – The N_2O catalytic reduction by methane over Cu-SBA -15 molar ratio (1:30) was studied based on physical mixture, impregnation method and pH adjustment method preparation. All catalytic reduction of N2O with methane were carried out in a flow reactor system at atmospheric pressure with 100 mL/min total flow was used. For the N_2O:CH_4 ratio effect, suggested that N_2O reacts with CH_4 is represented by $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$. The Cu/SBA-15 prepared by pH adjustment method has highest activity compared to Cu-SBA-15 prepared by impregnation method and physical mixture of CuO and SBA-15.

1. INTRODUCTION

Due to the increasing concern over environmental issues, studies on N_2O have oriented towards the development of catalytic systems for its elimination. Various types of catalysts have been reported to be active for the decomposition of nitrous oxide. Cu-SBA-15 is one of those materials showing better prospects for application as catalyst for N_2O decomposition [1-2]. Catalytic reduction is an alternative to catalytic decomposition with the potential to lower the temperature for effective N_2O removal by addition of a reducing agent. Therefore, the use of hydrocarbons as reducing agent is widely and easily available, such as CH_4, C_3H_6 or C_3H_8 required to meet commercial feasibility [3]. Previous report, the Cu/SBA-15 samples prepared by pH adjustment method shows higher activity on N_2O decomposition due to copper atom was substituted in the framework of the SBA-15 with better dispersion of copper species on mesoporous silica and easily reduced copper-silica support interaction CuO to Cu due to the weakening of copper - silica support interaction [2,4]. Known that, CH_4 is strong greenhouse-effect gases with a global warming potential (GWP) per molecule of about 20 times that of carbon dioxide. Therefore, it is interesting studies that a selective catalytic reduction (SCR) of N_2O by CH_4 is applied to simultaneous removal of N_2O and CH_4 in the emission gases by various Cu- SBA-15.

2. METHODOLOGY

2.1 Cu on SBA-15 preparation

For Cu on SBA-15 molar ratio (1:30) by the pH adjustment and impregnation samples was prepared based on previous report [2]. Meanwhile, physical mixture of copper oxide in SBA-15 samples was prepared by the required amount of powder form copper oxide was mixed together in one (1) gram of prepared SBA-15 to obtain Si:M molar ratios of 30:1.

2.2 N_2O decomposition and reduction with CH_4

The catalytic experiments were carried out in an alumina tube (4.76 mm i.d.) micro-reactor. Amount of 500.0 mg sample was filled into the tube to form a catalyst bed. The reaction temperature was monitored by a K-type thermocouple inserted inside the catalyst bed. The reaction unit was equipped with mass flow controllers and product analysis was performed with on-line gas chromatograph 7680A (Agilent) equipped with two columns in series (molecular sieve 5A and Heyasep Q) and TCD detector. For N_2O decomposition, the reaction gas composed of 1.0% N_2O in He at a total flow rate of 100 mL/min. Meanwhile for N_2O reduction with CH_4, reaction gas mixture was composed of 1.0 % N_2O and 0.1%,0.25% and 1% CH_4 in He at a total flow rate of 100 mL/min, respectively to N_2O:CH_4 ratio of 10:1, 4:1 and 1:1.

3. RESULTS AND DISCUSSION

3.1 Effect of different N_2O:CH_4 ratio

The effect of catalytic activity in the differences N_2O:CH_4 volume ratio on N_2O reduction reaction on Cu/SBA-15 (1:30) prepared by pH adjustment sample have been done. Figure 1 shows catalytic activity of N_2O reduction by CH_4 at different N_2O:CH_4 ratio compared to N_2O decomposition in the absence of CH_4. The catalytic activity of N_2O decomposition on Cu/SBA-15 catalyst was significantly promoted by the presence of CH_4. The conversions of CH_4 in different N_2O:CH_4 volume ratio reactions were compared in Figure 2, CH_4 conversion increased with the reaction temperature and with N_2O:CH_4 ratio. Meanwhile, Figure 3 shows the plotting graph N_2 and O_2 formation verses N_2O conversion at different N_2O:CH_4 ratio. The slope of the N_2O decomposition to CH_4 conversion is 4.0, 1.0 and 0.33, for N_2O:CH_4 ratio of 1:1, 4:1 and 10:1 respectively. Based on relationship of volume and mole of gases in Avogadgo Law, suggested that N_2O reacts with CH_4 is represented by $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$. Simultaneous presence of N_2O with CH_4 is essential for the high

selective catalytic reduction (SCR) activity of N_2O with CH_4. This is related to the high initial rate of CH_4 in N_2O + CH_4 reaction on Cu/SBA-15. The CH_4 plays an important role in the N_2O reduction, because the catalytic activities in N_2O conversion were drastically enhanced by the presence of CH_4. According to Nobukawa and Sugawara, nascent oxygen transients (O*) from N_2O dissociation before accommodation on stable adsorption sites can play an important role in activation and oxidation of CH_4. Thus, it seems that methane effectively reduced oxidized active sites (O*) and therefore increased the rate of the N_2O conversion [5].

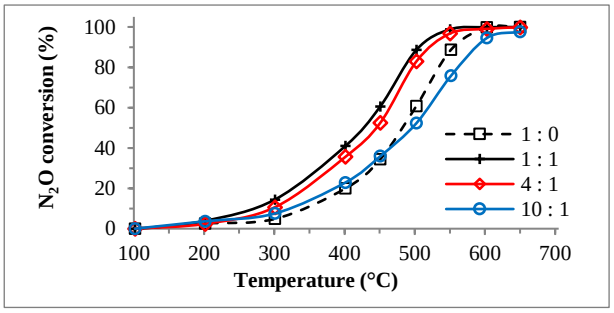

Figure 1 The catalytic activity of N_2O reduction by CH_4 on Cu/SBA-15 at different N_2O:CH_4 ratio.

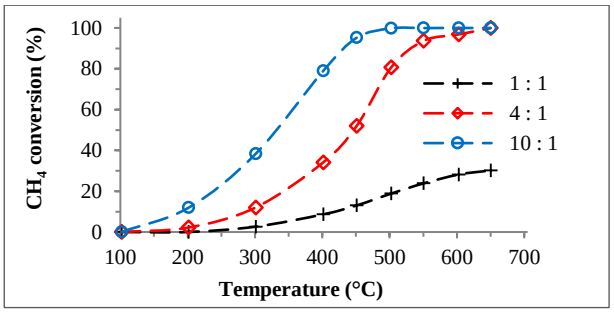

Figure 2 CH_4 conversion against Reaction temperature on different N_2O:CH_4 ratio.

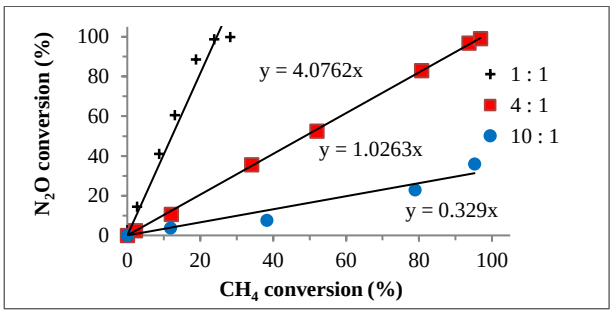

Figure 3 Plotting N_2O conversion verses CH_4 conversion on different N_2O:CH_4 ratio.

3.2. Catalytic activity of N_2O conversion

Figure 4 present N_2O decomposition on various copper on SBA-15. Cu/SBA-15 prepared through pH modification sample highest activity causing 80 % conversion at 550 °C. Cu on SBA-15 prepared by impregnation method and physical mixture samples show reached 80 % conversion at 650 °C.

Meanwhile, catalytic activity of N_2O reduction by CH_4 on various copper on SBA-15 was shows as in Figure 5. For Cu-SBA-15 impregnated, and CuO-SBA-15 physical mixture sample, the N_2O conversion curve was shifted to the left from SBA-15 pure sample. Both catalysts sample reached 100% conversion of N_2O at 600°C. Meanwhile, Cu/SBA-15 pH adjustment sample was much higher than other samples N_2O reduction by CH_4.

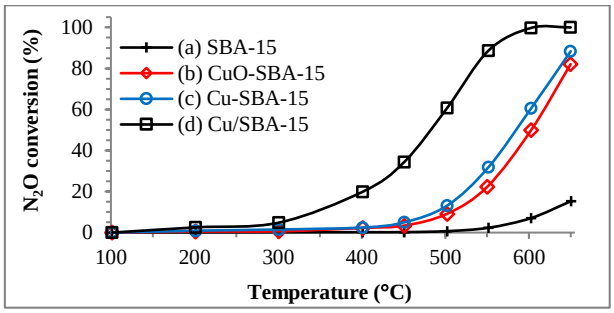

Figure 4 The catalytic activity of N_2O decomposition on (a) SBA-15, (b) CuO-SBA-15 (1:30) physical mixture, (c) Cu-SBA-15 (1:30) prepared by impregnated, and (d) Cu/SBA-15(1:30) prepared by pH modification.

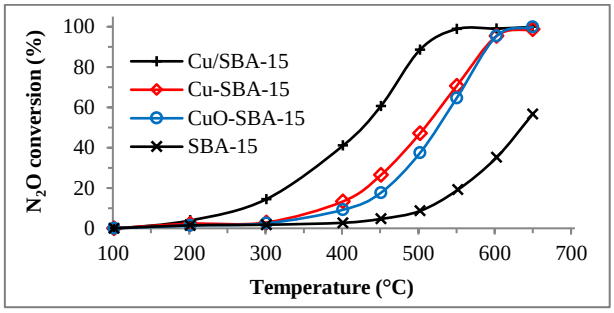

Figure 5 The catalytic activity of N_2O reduction by CH_4 at N_2O:CH_4 (1:1) volume ratio on various copper condition of (a) Cu/SBA-15 pH adjustment, (b) Cu-SBA-15 impregnated, (c), CuO-SBA-15 physical mixture and (d) SBA-15.

4. CONCLUSIONS

This paper has successfully demonstrated that the Cu/SBA-15 prepared by pH adjustment has highest activity compared to Cu-SBA-15 prepared by impregnation method and to physical mixture of CuO. Suggestion that N_2O reacts with CH_4 in this study is represented by $4N_2O + CH_4 \rightarrow 4N_2 + CO_2 + 2H_2O$.

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